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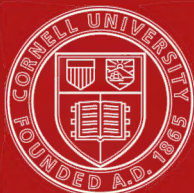
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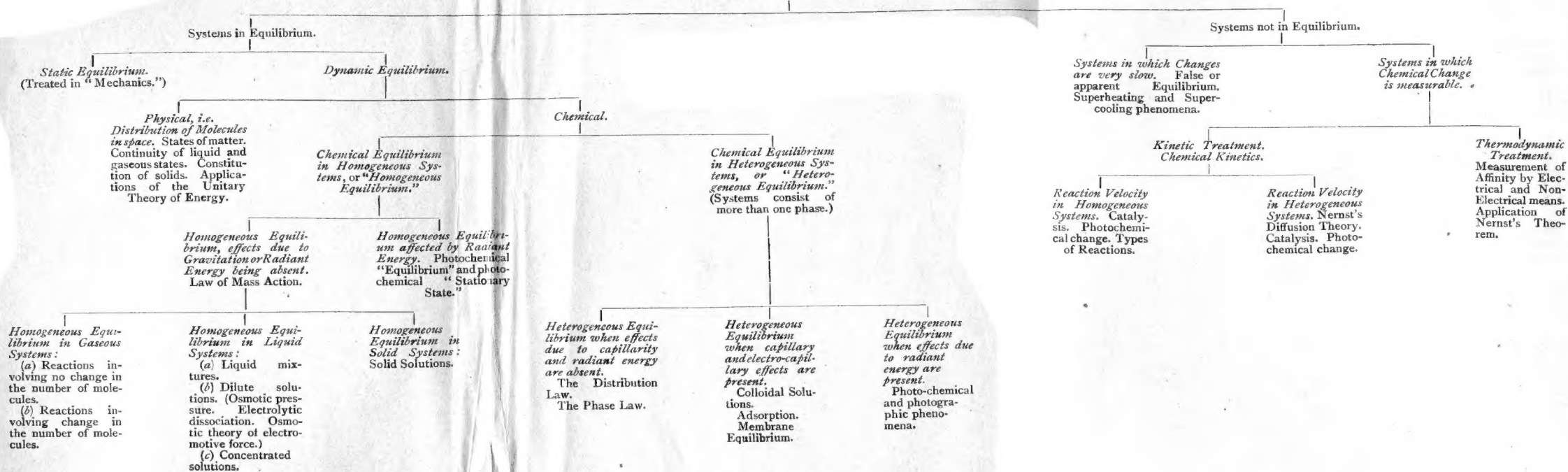
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A SYSTEM OF PHYSICAL CHEMISTRY

IN TWO VOLUMES

BY

WILLIAM C. McC. LEWIS, M.A. (R.U.I.), D.Sc.(Liv.)

BRUNNER PROFESSOR OF PHYSICAL CHEMISTRY IN THE UNIVERSITY OF
LIVERPOOL ; FORMERLY LECTURER IN PHYSICAL CHEMISTRY
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"SCIENCE is nothing without generalizations. . . . The suggestion of a new idea, or the detection of a law, supersedes much that had previously been a burden upon the memory, and by introducing order and coherence facilitates the retention of the remainder in an available form."

LORD RAYLEIGH.

PREFACE

THIS book is intended to be used as a general textbook of physical chemistry by those who already possess some knowledge of both physics and chemistry. As there are at the present time several excellent treatises on elementary physical chemistry in English, it would obviously be fulfilling no good purpose to simply add another covering much the same ground. I have therefore aimed at making this book fairly comprehensive by including as far as was feasible some account of recent investigation, such for example as: the structure of the atom, the theory of concentrated solutions, capillary chemistry, Nernst's theorem of heat, the thermodynamics of photochemical reactions, and the application of the Planck-Einstein "Energie Quanta" to the specific heat of solids. Besides these recently examined problems, about which there is still considerable speculation, the fundamental principles and their applications which find a place in other books have likewise been incorporated here. At the same time I would suggest to the reader the advisability of first familiarizing himself with the broad outlines of the subject, such as will be found, for example, in Walker's *Introduction to Physical Chemistry* or Senter's *Outlines of Physical Chemistry*.

The title which has been employed requires, perhaps, a word of explanation. The "System" consists in regarding all physico-chemical phenomena as being capable of separation into two classes: first, phenomena exhibited by material systems when *in* a state of equilibrium; and, secondly, phenomena exhibited by material systems which have *not* reached a state of equilibrium. It is clear that this is not only a perfectly

natural division, but likewise a perfectly general one, since any conceivable material system must belong to one class or the other. By emphasizing this idea I hope to have impressed upon the reader's mind the fundamental co-relations which exist between what might at first sight appear very widely different phenomena. It has been my endeavour to get as far away as possible from the "selected chapter" method of treatment, which however necessary and suitable in a preliminary accumulation of facts, is very liable to cause the student to lose sight altogether of the essential unity of his subject.

The scientific treatment of any set of phenomena consists in applying the minimum of general principles or theories which can afford a reasonable explanation of the behaviour of matter under given conditions, and predict its behaviour under new conditions. The principles referred to as far as physics and chemistry are concerned are the kinetic theory and thermodynamics. In the kinetic method of treatment emphasis is laid upon the actual molecular mechanism of a given process; in the thermodynamic method the emphasis is laid upon the energy changes involved. Both methods should be familiar to anyone who undertakes the task of original investigation. Since a knowledge of the fundamental laws of the kinetic theory (including statistical mechanics), and thermodynamics is of such importance, some account—necessarily brief—has been given in this book. Of course, one might commence by writing an introductory chapter dealing with these various principles and then proceed to apply them indiscriminately to the phenomena dealt with. Anyone with teaching experience, however, will appreciate the fact that this method has the very serious drawback of bringing the reader at an early stage into contact with what is certainly the most difficult part of the subject, namely, the fundamental principles of thermodynamics and statistical mechanics. I have therefore divided the book into three parts, in which the phenomena exhibited by systems in equilibrium and not in equilibrium are treated, first, from the "classical" kinetic standpoint only; then independently

from the thermodynamic; and finally from the standpoint of thermodynamics and the new or "modified" principles of statistical mechanics. I would only like to repeat that the "system" of classification upon which this book is based does *not* consist in the division into parts just mentioned, which latter is a purely arbitrary division and is only introduced for the purpose of making the book as readable as possible from the student's point of view. Further it has been found desirable to divide the work into two volumes. Vol. I. contains Part I., and is briefly entitled "Kinetic Theory"; Vol. II. contains Parts II. and III., and is entitled "Thermodynamics and Statistical Mechanics."

As regards the thermodynamical treatment, it will be seen that the concept of "maximum work" and "free energy" has been employed practically to the exclusion of others. I have found by experience that this is more easily grasped than the idea of entropy, although I suppose that ultimately this must be something of a mental delusion.

Another feature to which I should like to draw attention is the intentional employment of the investigator's actual words where this is at all possible. It seems to me that in ascribing any scientific statement to an author it is only fair to reduce the editorial condensation process to a minimum. Of course, scientific papers as they appear in the journals are, as a rule, unsuitable for direct incorporation into a book of this nature and size, but I have attempted to reproduce them, at least in part, in the case of a few of the *classic* papers in physical chemistry with which one associates the names of van 't Hoff, Ostwald, Arrhenius, and Nernst. Nowadays one expects that the language difficulty will not be a serious one in the matter of reading foreign memoirs; though any one who wishes to read these classic memoirs in their entirety in English will find a few of them scattered through the *Philosophical Magazine*, or more readily available in Harper's Scientific Memoir Series, edited by Ames.

As regards the subject-matter actually dealt with in this book, it will be observed that the relations of physical properties

to chemical constitution and other purely stoichiometrical relations have been omitted, since in my opinion a proper appreciation of what has been done here can only be obtained through the medium of a volume specially devoted to the subject, in which there is sufficient space for the comparison of a large collection of numerical data, such as one finds, for example, in S. Youngs' *Stoichiometry* and S. Smiles' *Relation of Chemical Constitution to some Physical Properties*.

As this is one of the series of textbooks edited by Sir William Ramsay, I have not hesitated to avail myself of those already published in the matter of many of the illustrative examples. I have also given numerous references where further information upon any subject is desirable not only to this series but still more to the original papers themselves.

In addition to references in the text itself, I should also like to acknowledge in this place my indebtedness to other works already published, namely: Ostwald's *Lehrbuch*, Nernst's *Theoretical Chemistry*, Nernst's *Applications of Thermodynamics to Chemistry*, van 't Hoff's *Lectures*, Haber's *Thermodynamics of Technical Gas Reactions*, Walker's *Introduction to Physical Chemistry*, Lehfeldt's *Textbook of Physical Chemistry*, Abegg's *Electrolytic Dissociation Theory*, Arrhenius' *Electrochemistry*, Arrhenius' *Theories of Chemistry*, Le Blanc's *Electrochemistry*, Sackur's *Chemische Affinität* (Wissenschaft Series), Sackur's *Thermochemie und Thermodynamik*, Knox's *Physico-Chemical Calculations*, Kuenen's *Die Zustandsgleichung der Gase und Flüssigkeiten* (Wissenschaft Series), Bancroft's *Phase Rule*, Sir J. J. Thomson's *Electricity and Matter*, Sir J. J. Thomson's *Corpuscular Theory of Matter*, Preston's *Heat*, Freundlich's *Kapillarchemie*, Drude's *Optics*, Risteen's *Molecules and Molecular Magnitudes*, Perrin's *Brownian Movement and Molecular Reality*, Weigert's *Chemische Einwirkung des Lichtes* (Ahren's Sammlung), N. Campbell's *Modern Electrical Theory*. As regards symbols, I have employed to a considerable extent those recommended by the International Commission for the Unification of Physico-Chemical Symbols (1914). For this

information I am indebted to the Secretary of the Committee, Professor Alexander Findlay.

I would also take this opportunity of expressing my warmest thanks for the assistance which I have received on various occasions from my colleagues and friends, Professor F. G. Donnan, F.R.S., University College, London; Professor A. W. Porter, F.R.S., University College, London; Professor N. T. M. Wilsmore, University of Western Australia, Perth; and Professor W. B. Morton, Queen's University, Belfast.

TABLE OF CONTENTS OF VOLS. I AND II

Chart indicating the general system or scheme of subdivision

PAGE

Frontispiece

VOLUME I

PART I

CONSIDERATIONS BASED UPON THE KINETIC THEORY

CHAPTER I

Introductory—Molecules, atoms, and electrons—Elements of the kinetic theory—Molecular reality—Radioactivity—Transmutation of the elements 1

CHAPTER II

Distribution of molecules in space—Physical equilibrium—The continuity of the liquid and gaseous states from the kinetic standpoint 72

CHAPTER III

Chemical equilibrium in homogeneous systems from the kinetic standpoint—Gaseous systems—Deduction of the law of mass action—Reactions in gaseous systems involving no change in the total number of molecules—Reactions involving a change in the number of molecules—Effect of change of temperature and pressure upon the equilibrium constant 129

CHAPTER IV

Chemical equilibrium in homogeneous systems (<i>continued</i>)—Liquid mixtures—Solutions—Properties of solutions	PAGE 182
--	-------------

CHAPTER V

Chemical equilibrium in homogeneous systems (<i>continued</i>)—Mechanism of electrolytic conduction in solutions—The theory of electrolytic dissociation in aqueous solutions—Electrolytic dissociation in non-aqueous solutions	223
--	-----

CHAPTER VI

Chemical equilibrium in homogeneous systems (<i>continued</i>)—Solid solutions	341
--	-----

CHAPTER VII

Chemical equilibrium in heterogeneous systems from the kinetic standpoint (effects due to capillarity, radiation, etc., being absent)—Nernst's Distribution Law—Gas-liquid systems—Liquid-liquid systems—Gas-solid systems—Solid-solid systems—Solid-liquid systems—Solubility and "solubility product"	348
---	-----

CHAPTER VIII

Chemical equilibrium in heterogeneous systems modified by capillary and electro-capillary effects—Colloidal solutions	395
---	-----

CHAPTER IX

Systems not in equilibrium—Treatment from the kinetic standpoint— <i>Homogeneous systems</i> : Diffusion of solutes in a solution—Reaction velocity—Types of reactions—Catalysis	421
--	-----

CHAPTER X

Systems not in equilibrium— <i>Heterogeneous systems</i> : Nernst's theory of reaction velocity—Catalysis	489
---	-----

SUBJECT INDEX	511
-------------------------	-----

AUTHOR INDEX	518
------------------------	-----

(END OF VOLUME I)

VOLUME II

PART II

CONSIDERATIONS BASED UPON THERMODYNAMICS

CHAPTER I

	PAGE
Introductory—Elementary consideration of the principles of thermodynamics	I

CHAPTER II

Introductory—Further consideration of thermodynamic principles	49
--	----

CHAPTER III

Continuity of the liquid and gaseous states from the thermodynamic standpoint	75
---	----

CHAPTER IV

Thermodynamic criteria of chemical equilibrium in general	111
---	-----

CHAPTER V

Chemical equilibrium in homogeneous systems from the thermodynamic standpoint—Gaseous systems—Deduction of the law of mass action—The van 't Hoff isotherm—Principle of "mobile equilibrium" (Le Chateliér and Braun)—Variation of the equilibrium constant with temperature and pressure	132
---	-----

CHAPTER VI

Chemical equilibrium in homogeneous systems—Dilute solutions—Applicability of the gas laws—Thermodynamic relations between osmotic pressure and the lowering of vapour pressure, the rise of boiling-point, the lowering of freezing point of the solvent, and change in the solubility of the solvent in another liquid—Molecular weight of dissolved substances—Law of mass action—Change of equilibrium constant with temperature and pressure	150
---	-----

CHAPTER VII

Chemical equilibrium in homogeneous systems—Dilute solutions (<i>continued</i>)—Outlines of the electrochemistry of dilute solutions	174
--	-----

CHAPTER VIII

	PAGE
Chemical equilibrium in homogeneous systems—Concentrated solutions	216

CHAPTER IX

Chemical equilibrium in heterogeneous systems in the absence of electrical, capillary, or gravitational effects—The Phase Rule and some of its applications—The theory of allotropy	238
---	-----

CHAPTER X

Chemical equilibrium in heterogeneous systems from the thermodynamic standpoint when capillary or electrical effects are of importance—Adsorption—Donnan's theory of membrane equilibria	303
--	-----

CHAPTER XI

Systems not in equilibrium from the thermodynamic standpoint—Affinity and its measurement by means of vapour pressure, solubility, and electromotive force—Oxidation and reduction processes—Change of affinity with temperature	320
--	-----

CHAPTER XII

Systems not in equilibrium (<i>continued</i>)—Relation between the affinity and the heat of a reaction—Nernst's heat theorem and some of its applications	357
---	-----

PART III

CONSIDERATIONS BASED UPON THERMODYNAMICS
AND STATISTICAL MECHANICS

CHAPTER I

Behaviour of systems (in equilibrium and not in equilibrium), exposed to radiation—Photochemistry—Thermodynamic treatment of photochemical reactions	397
--	-----

CHAPTER II

Applications of the Unitary Theory of Energy (Energy-quanta) to physical and chemical problems	463
--	-----

SUBJECT INDEX	543
-------------------------	-----

AUTHOR INDEX	549
------------------------	-----

A SYSTEM OF PHYSICAL CHEMISTRY

PART I

CONSIDERATIONS BASED UPON THE KINETIC THEORY

CHAPTER I

Introductory—Molecules, atoms, and electrons—Elements of the Kinetic Theory—Molecular reality—Radioactivity—Transmutation of the elements.

THE KINETIC MOLECULAR THEORY OF THE CONSTITUTION OF MATTER.

It would be futile within the limits of an introductory chapter to attempt to give any concise account of the kinetic theory of matter. The student is assumed to be familiar with the general outlines of the subject, especially as regards the gaseous state. For the sake, however, of allowing us to gain some quantitative ideas of the processes which occur in molecular, and in general, in chemical processes it will be advantageous to present at least some of the numerical *results* which have been obtained. For further information the reader is referred to Meyer's *Kinetic Theory of Gases*, translated by Baynes; Jeans' *Dynamical Theory of Gases*; and Byk's *Kinetische Theorie der Gase*.

§ I

SOME OF THE MORE IMPORTANT MAGNITUDES IN MOLECULAR PHYSICS, PRIOR TO THE WORK OF EINSTEIN, PERRIN, SVEDBERG, AND MILLIKAN.

According to the molecular theory, all matter is composed of small particles or molecules which are in rapid and irregular

motion, the amplitude of such motion mainly determining whether the matter exists in the solid, liquid, or gaseous *state*. As is well known, the gaseous state, in which the molecules are on the average farther apart than in the other states, and likewise in more violent motion,¹ has lent itself most readily to theoretical treatment. For this reason we shall, to a large extent, limit ourselves to a brief consideration of the gaseous state. The first magnitude of interest is the *mean free path* of a molecule, that is the average distance traversed by a molecule between two successive collisions with other molecules. In a gas this is very large compared with the actual dimensions of the molecules themselves. In liquids and solids, on the other hand, the mean free path is of much the same order of magnitude as the molecular diameter itself. The next magnitude to be considered is the *velocity* of the molecules. The molecules in a gas do not all possess the same velocity. Even if this were momentarily the case, it can be shown on the theory of probability that the collisions would quickly destroy the equality. The enormous number of molecules even in a cubic millimetre of gas precludes any attempt to deal with the velocities of the individual molecules. The best we can do is to obtain a value for the *average velocity*. The problem of the distribution of velocities amongst the molecules of a gas has been solved in general terms by Clerk Maxwell in the theorem named after him.

STATEMENT OF MAXWELL'S THEOREM OF DISTRIBUTION OF VELOCITIES.

If we consider a system consisting of elastic spheres, *i.e.* molecules, in motion, the result of such motion will be to set up a certain state called a statistical equilibrium, such that the number (dn) of spheres having velocities lying between \bar{v} and $(\bar{v} + d\bar{v})$ is given according to Maxwell by the relation—

$$dn = \frac{4n}{a^3\sqrt{\pi}} \cdot e^{-\frac{\bar{v}^2}{a^2}} \cdot \bar{v}^2 d\bar{v} \quad . \quad . \quad . \quad (1)$$

¹ This must not be taken as meaning necessarily greater *energy* of translation.

where n denotes the total number of spheres in the system, e is the base of natural logarithms, and a is a constant. We have to distinguish two closely related terms, namely, the mean or *average velocity* \bar{v}_0 , which is simply the sum of all the velocities at a given moment divided by the number of molecules, and, secondly, the *root-mean-square-velocity* denoted by u . This quantity is such that its square is the sum of the squares of each separate velocity divided by the number of molecules.

That is
$$u^2 = \frac{\bar{v}_1^2 + \bar{v}_2^2 + \bar{v}_3^2 + \text{etc.}}{n}$$

It can be shown that u and \bar{v}_0 are connected by the relation—

$$\bar{v}_0 = \frac{4}{\sqrt{6\pi}}u = 0.9213u$$

That is, the average velocity is nearly, but not quite, so great as the root-mean-square-velocity. The importance of the latter term is apparent when we remember that the kinetic energy of a molecule whose mass is m is given by the expression $\frac{1}{2}mu^2$.

We can best illustrate the Maxwell Theorem, which is simply equation (1), by means of a graph (Fig. 1) in which

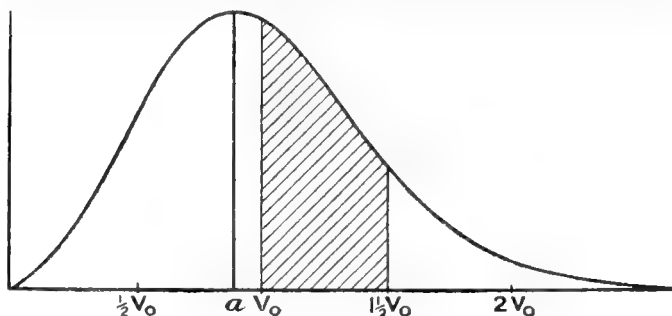


FIG. 1.

the ordinates denote number of molecules or rather fractions of the total n , and the abscissæ denote velocities. The ordinate for any value of \bar{v} is proportional to the number of

molecules having a velocity between \bar{v} and $(\bar{v} + d\bar{v})$. It will be observed that the greater majority of the molecules present in the system are represented by an area the limits of which are not very different from \bar{v}_0 , the average value. Since the curve approaches the horizontal axis asymptotically on each side of the maximum, we can infer that there are a very few molecules practically motionless, and likewise a very few with extremely great velocity. This latter fact ought to be borne in mind from the chemical standpoint as possibly of importance in connection with the phenomenon of catalysis.

DEFINITION OF TEMPERATURE FROM THE KINETIC STANDPOINT.

According to the kinetic theory the temperature of a system corresponds to a certain value of the mean kinetic energy of translation of the molecules, namely, $\frac{1}{2}m\bar{v}^2$; so that if the temperature of a body be kept constant, the mean kinetic energy of the molecules is likewise constant. The reasonableness of this assumption is clearer if we consider the process of cooling a body. On this view, cooling a body is the same thing as decreasing the kinetic energy of the molecules, and one might imagine the cooling process continued until the translational motion of the molecules would finally cease. At this point the system has reached what is known as the "*absolute zero*" of temperature. With the help of the kinetic theory applied to the thermal expansion of gases we can calculate that the absolute zero is 273° below the freezing point of water, or simply -273° C. The behaviour of matter at this point is practically inconceivable to us, although one must not imagine that even at the absolute zero the body possesses no energy at all. It certainly possesses no kinetic energy in the form of translation. The question of the energy possessed by a substance at the absolute zero will be taken up in connection with Nernst's Heat Theorem (Part II. (Vol. II.), Chap. XII.) as well as in connection with the "Unitary Theory of Energy" (*cf.* Part III., (Vol. II.)).

THE PRESSURE EXERTED BY A GAS. BOYLE'S LAW, CHARLES' OR GAY-LUSSAC'S LAW, AND THE HYPOTHESIS OF AVOGADRO.

The following is not a rigid proof of Boyle's Law, but it is at least approximately correct.

Consider a large mass of gas at a given temperature, and suppose that a unit cube of the gas contains n molecules. The molecules are supposed all to possess the same velocity u . The mass of each molecule is m . The molecules move in all directions in the actual case, but for simplicity we shall consider that they may be divided into sets. For the moment we are regarding the walls of the cube as impermeable to the gas. Consider one molecule starting from one wall of the cube and moving in a straight line perpendicularly to the opposite wall where it rebounds, the change of momentum being $2mu$. Since the velocity is u , the molecule traverses u cms. per second, or passes over 1 cm., that is from wall to wall, u times in one second. That is, it strikes the wall u times per second,¹ and hence the total change in momentum per second is $2mu^2$. If there are n molecules present in the cube, we can imagine equal numbers to be travelling towards each of the six walls at the same instant.

That is, at any instant $\frac{n}{6}$ molecules are travelling towards a certain wall, and when they strike they exert pressure on that wall. The total change in momentum per second due to the molecules striking one wall is $\frac{n}{6} \times 2mu^2$ or $\frac{1}{3}nmu^2$. Since the

¹ Actually the molecule which starts from the right-hand side strikes the left-hand wall once every *two* seconds and the right-hand wall just as often. This would make the number of collisions per second upon the left-hand wall due to this particular molecule only $\frac{u}{2}$. During the same

second this molecule has, however, bombarded the right-hand wall $\frac{u}{2}$ times also, and every molecule may be regarded as thus striking two walls $\frac{u}{2}$ times *each* per second. Evidently the total bombardment is just equivalent to each molecule striking *one* wall only (say the left) u times per second.

wall is of unit area the force exerted upon it is identical with the pressure p of the gas. Hence, we obtain the relation

$$p = \frac{1}{3}nm\bar{u}^2$$

Further, since nm represents the total mass of the gas in the unit cube, the quantity $\frac{nm}{1}$ c.c. is simply the density ρ of the gas, and therefore one may write—

$$p = \frac{1}{3}\rho\bar{u}^2$$

Also since the density ρ is the ratio of the total mass of gas M (which occupies the volume v) to the volume v , we can write

$$p = \frac{1}{3}\frac{M}{v}\bar{u}^2, \text{ or } pv = \frac{1}{3}M\bar{u}^2$$

But if the temperature of the gas be kept constant its total kinetic energy, which is $\frac{1}{2}M\bar{u}^2$, is likewise constant, and hence $\frac{1}{3}M\bar{u}^2$ is necessarily constant, so that one obtains—

$$pv = \text{constant}$$

which is Boyle's Law for gases. Further, Charles' or Gay-Lussac's Law for gases states that if the pressure of a given mass of gas be kept constant and the temperature be altered, the volume changes in proportion to the temperature change; or what amounts to the same, if the volume be kept constant the pressure varies as the (absolute) temperature. Boyle's and Charles' Laws may be expressed thus—

$$\frac{pv}{T} = \text{constant}$$

and this expression follows at once from that already deduced upon the basis of the kinetic theory, according to which $\frac{1}{2}M\bar{u}^2$, and therefore $\frac{1}{3}M\bar{u}^2$, is proportional to the absolute temperature T , so that we can write $p v = \text{constant} \times T$

or
$$\frac{pv}{T} = \text{constant}$$

Avogadro's Hypothesis may likewise be shown to be in agreement with the kinetic theory. According to this hypothesis,

equal volumes of any gases at the same temperature and pressure contain the same number of molecules. Consider any two gases. The pressure p exerted by the first at a given temperature may be written

$$p = \frac{1}{3}n_1m_1u_1^2$$

where n_1 is the number of molecules in unit volume, m_1 is the mass of each molecule, and u_1^2 the mean square velocity of the molecules. Similarly, the same pressure p exerted by the second gas may be written—

$$p = \frac{1}{3}n_2m_2u_2^2$$

Hence

$$n_1m_1u_1^2 = n_2m_2u_2^2$$

Since the gases are likewise at the same temperature, the mean kinetic energies of the molecules of each gas are the same; that is

$$\frac{1}{2}m_1u_1^2 = \frac{1}{2}m_2u_2^2$$

Combining these two equations, one finds that

$$n_1 = n_2$$

That is, the number of molecules in unit volume (*i.e.* the same volume for each gas) is the same for both, which is Avogadro's Hypothesis.

THE AVERAGE MOLECULAR VELOCITIES IN VARIOUS GASES AT 0°C.

It is found as a result of experiment that under *normal* conditions—that is under one atmosphere pressure and at 0° C.—the density of hydrogen gas is very nearly 0.00009 gram per cubic centimetre. The expression

$$p = \frac{1}{3}\rho u^2$$

may thus be employed for the calculation of u , viz. :

$$= \sqrt{\frac{3p}{\rho}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

All numerical values must of course be expressed in the same units (the C.G.S. system). In the case of hydrogen gas under *normal* conditions, $p = 1$ atmosphere $= 1.016 \times 10^6$

dynes per square centimetre, $\rho = 9 \times 10^{-5}$ grams per cubic centimetre, and hence

$$u = 1.8 \times 10^5 \text{ cms. per second.}$$

The average value \bar{v}_0 of the velocity is $0.91213u$, so that \bar{v}_0 for hydrogen at 0°C. and 760 mm. is $1.65 \times 10^5 \text{ cms. per second.}$ Other gases such as oxygen, nitrogen, and carbon dioxide have molecular velocities one-fourth to one-tenth of that possessed by the hydrogen molecule.

VISCOSITY OF GASES AND THE CALCULATION OF THE MEAN FREE PATH OF THE MOLECULES.

If a layer in a gas is caused to stream in any given direction, one may anticipate that owing to the frequent collisions between the molecules of the streaming layer and the contiguous molecules of the surrounding gas that the streaming motion would be partially transferred to the "stationary" gas layers, and as a whole the gas would begin to stream, except that layer which lay closest to the walls of the vessel. A certain amount of momentum has been transferred through the various layers of the gas, and hence in virtue of the streaming motion the molecules have exerted a force upon one another. This force is called viscosity. Viscosity is possessed even by a perfect gas, *i.e.* one which obeys Boyle's Law absolutely. This force is therefore not to be confounded with the forces of molecular attractions which, as we shall see later, are present in all actual gases and cause them to depart to greater or less extents from the ideal or perfect gas. Viscosity is sometimes called *internal friction*, and the coefficient of viscosity of any fluid—liquid or gas—is defined as the force per unit area exerted between two parallel layers, 1 cm. apart, when the velocity of streaming differs by unity in the two layers.

With the help of the kinetic theory it is possible to deduce a relation between the coefficient of viscosity η of a gas, and the mean free path λ , according to which—

$$\eta = \frac{1}{3}\rho\lambda u \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(see Meyer's *Kinetic Theory of Gases*, pp. 175 *seq.*), where ρ is density and u velocity.¹

Now we have already seen that the pressure p of the gas is given by—

$$p = \frac{1}{3}\rho u^2$$

so that the above expression may be rewritten—

$$\lambda = \eta \sqrt{\frac{3}{p\rho}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It can be shown on theoretical grounds that the viscosity of a gas is independent of the pressure which, though by no means an obvious result, has been completely verified by experiment.

For the present purpose, however, the importance of viscosity determinations lies in the fact that they permit of a calculation of the mean free path of the molecules—for example, by means of equation (4).

In the following table are given the coefficients of viscosity, the mean free paths, and the collision frequencies of a few gases (see Meyer's *Kinetic Theory*, p. 192). The collision frequency is the mean free path λ divided by the root-mean-square-velocity u .

Gas.	η .	λ cms.	Collision frequency, or number of collisions per second, $\times 10^{-6}$
Hydrogen	0·0486	0·04182	9280
Nitrogen	0·03166	0·04094	4820
Oxygen	0·03187	0·04100	4280
Carbon dioxide . .	0·03138	0·04063	5780
Carbon monoxide . .	0·03162	0·04092	4920

Reference will be made later to Rankine's determinations of the relative viscosities of the rare gases (A. O. Rankine, *Proc. Roy. Soc.*, 83, 516, 1910).

¹ It should be borne in mind that the u term for any gas is always very much greater than any streaming velocity which can be artificially set up.

MOLECULAR ATTRACTION IN GASES AND THE EFFECTIVE RANGE OF ATTRACTION.

Hitherto we have considered gases simply as systems of small spherical perfectly elastic particles in rapid motion, colliding frequently, but otherwise without influence upon one another. The study of actual gases has, however, shown that these assumptions are only approximately, not absolutely fulfilled (see Chap. II.). Boyle's Law, for example, at high pressures does not hold accurately even for gases such as hydrogen, oxygen, nitrogen, etc., which at ordinary temperatures are far above their liquefying points. As will be seen later, these and other discrepancies are attributable to two causes, one of which is the existence of attractive forces between the molecules of the gas, and the other is the magnitude and actual compressibility of the molecules themselves, which under high pressure can no longer be regarded as occupying a space which is negligible compared with the free space between them. The attractive forces referred to are only effective throughout an extremely small range, approximately 10^{-7} to 10^{-8} cm. Inside this range, however, the attractions may become enormously great. This effective range is known as "the range of molecular attraction." Of course, these forces are exerted theoretically to an infinite distance throughout space, but it is only within the extremely narrow limits mentioned that the attraction due to a molecule assumes any magnitude of importance. In the case of liquids, where the average distance apart of the molecules is less than the range of attraction, these forces may amount to several hundreds or even thousands of atmospheres reckoned across any unit area in the interior. To this is to be attributed the decreased freedom of motion possessed by the molecules of a liquid as compared with the molecules of a gas, and consequently the complete inapplicability of the simple gas laws.

The most direct means of showing that ordinary gases are not *perfect* or *ideal*—though nearly so—is afforded by the well-known porous plug experiment of Joule and Thomson (Lord Kelvin). In this experiment a gas is passed under high

pressure through a porous plug, at the other side of which the pressure is kept low. Under these conditions it was shown by Joule and Thomson that the temperature of the gas differed on the two sides of the plug. For all ordinary gases except hydrogen the temperature on the low-pressure side was lower than that on the high-pressure side. In the case of hydrogen, the temperature effect was the reverse, but this was later shown to be due to the actual mean temperature of the experiment being too high for that gas. If the experiment be carried out at a very low mean temperature, hydrogen is found to behave like other gases. If these gases had been ideal gases, no change in temperature on passing through the plug would be expected.

Numerous attempts have been made from time to time to find out the law of molecular attraction, that is, how the force varies with the distance. It is certain that the law is not that which governs gravitational attraction, in which the force varies inversely as the square of the distance. Reference will only be made in the present instance to the law of attraction, which is involved in van der Waals' equation for fluids (Chap. II.). If we consider a unit area in the interior of a fluid, the force of attraction across the area depends upon the number of molecules spread over the unit surface, and likewise upon the distance apart of the molecules. If r is the average distance apart of the molecules, then the number of molecules per unit area is inversely proportional to r^2 , and as the attractive force between any two molecules on opposite sides of the area varies inversely as some unknown function of the distance apart which we may write in the form r^n , it follows that the attractive force exerted per unit area perpendicularly across the imaginary plane is proportional to $\frac{1}{r^{n+2}}$. Since the volume v of the fluid is proportional to r^3 , the attractive force may be written as proportional to $\frac{1}{v^{\frac{n+2}{3}}}$. But according to van der Waals' equation, this force can be expressed by the term $\frac{a}{v^2}$, where a is a constant. To make these two expressions

concordant, it is necessary that we put $n = 4$. That is, the van der Waals' equation assumes that *the attraction between molecules varies inversely as the fourth power of the distance of the molecules apart*. It may be mentioned that under certain conditions electrical (and magnetic) attractions¹ vary as this power (not simply as the inverse square). If we assume with Sutherland (*Phil. Mag.* [6], 4, 625, 1902) and Reinganum (*Physikal. Zeitschr.*, 2, 241, 1901; Drude's *Annalen*, 10, 334, 1903) that equal positive and negative charges are present in molecules, and these charges are concentrated wholly or partly in points, then the molecule will represent what is known as an "electrical doublet," and the inverse fourth-power law will hold good for such a system, just as it does in the case of two small magnets.

From this point of view it would seem, therefore, that molecular attraction may be ultimately electrical in origin. It must be pointed out, however, that it is by no means certain that the inverse fourth-power law is the correct one. Inverse fifth- and even sixth-power laws have been found to be fairly applicable, so that there is doubt as to whether these molecular attractions can be expressed in this simple "power" form at all. For a further discussion of the question of molecular attraction reference is made to Sutherland's earlier papers (*Phil. Mag.*, 22, 81, 1886; 27, 305, 1889; 35, 211; 36, 150, 507, 1893), as well as to the chapter upon the subject in J. P. Kuenen's *Die Zustandsgleichung der Gase und Flüssigkeiten* (Wissenschaft Series).

We now pass on to the question of the determination of the *range* of molecular attraction.

The most frequently employed value, namely, 5×10^{-8} cm., is that which is obtained by Quincke's "Wedge" method. This value is approximately 100 to 200 times greater than the actual diameters of the molecules of ordinary fluids. By comparison with other results, however, it appears likely that Quincke's estimate is certainly too large. A better method consists in measuring the limiting thickness

¹ As regards possible electromagnetic attraction, cf. W. C. McC. Lewis, *Phil. Mag.*, June, 1914.

of a stable soap film which was carried out by Reinold and Rücker (*Phil. Trans.*, 177, part II., 627, 1886). Two cylindrical soap films were obtained by means of the apparatus shown diagrammatically in Fig. 2.¹ One film could be main-

tained at constant thickness (by passing an electrical current through it vertically upward) and therefore at constant surface tension, while the other was allowed to drain, producing changes in the thickness, which should be indicated by changes in the surface tension when the film has thinned down to the region of the

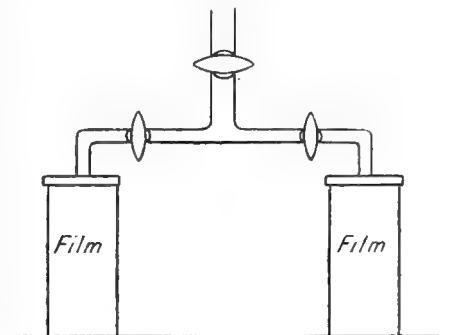


FIG. 2.

molecular range of attraction. Any change in the surface tension would be immediately indicated by a bulging of one of the cylinders and a contraction of the other. It was found that the tension was constant down to the stage of tenuity when the film was showing the black of the first order of Newton's scale of colour. By measurements of optical interference as well as by electrical measurements, Reinold and Rücker were able to calculate the thickness of the black film and found it to be $12\mu\mu$ or 12×10^{-7} cm. This might at first sight appear to be a fairly accurate value for the range of attraction, but this is rendered much less conclusive owing to the existence of certain phenomena observed by Reinold and Rücker themselves. Thus it was shown that the black and coloured parts of the film were *sharply* separated, so that the film is really discontinuous, in some places the thickness is 250 times that in others (*i.e.* the black portions), and yet apparently the film as a whole is in equilibrium. This suggests that between $12\mu\mu$ and $100\mu\mu$ the film is

¹ For a more detailed account, see Poynting and Thomson, *Properties of Matter*.

unstable, but is stable at either limit. On allowing the film to drain still further, so that the thinnest parts were less than $12\mu\mu$, these parts became unstable. Later, Johonnot (*Phil. Mag.*, 47, 501, 1899) showed in the case of sodium oleate films that the black part itself consists of two portions, one $12\mu\mu$ thick, the other $6\mu\mu$. The general result of these very complex phenomena appears to be that the attraction exerted by a molecule ceases to be effective at a distance of $5 - 10 \times 10^{-7}$ cm.

Mention should also be made of a calculation carried out by Lippman, based upon electro-capillary observations (*Comptes Rendus*, 95, 686, 1882). Lippman obtained the value 3×10^{-8} cm. for the thickness of the "electrical double layer" (see Chap. VIII. on Capillary Effects) at the interface, where the mercury and sulphuric acid solution met; and we may possibly identify this with the range of molecular attraction. Assuming this to be the case, and introducing one or two obvious corrections into Lippman's calculation, one obtains the value 2.4×10^{-7} cm. More recent work of the writer (Lewis, *Phil. Mag.*, Jan., 1913, p. 61) leads to the conclusion that the range is of the order 10^{-8} cm.

ATTEMPTS TO DETERMINE THE ACTUAL DIMENSIONS OF MOLECULES. (See Jeans, *Dynamical Theory of Gases*.)

(1) An early attempt to determine the aggregate volume occupied by the molecules of a gas consisted in applying the expression—

$$K = \frac{1 + 2\epsilon}{1 - \epsilon}$$

where K is the dielectric constant of the gas, and ϵ is the ratio which the actual volume of the molecules bears to the observed volume. The expression is based on the Clausius-Mosotti theory of dielectrics, and the molecules are assumed to be conductors. Mercury vapour would probably correspond to these conditions, but its dielectric constant is not known. Although it is straining the applicability of the expression, it has been employed in connection with a number

of gases, including the rare gases of the atmosphere. According to the Maxwell theory of light, we can write—

$$K = \mu^2$$

where μ is the refractive index of the gas for very long waves. Substituting this in the above expression, one obtains—

$$\epsilon = \frac{\mu^2 - 1}{\mu^2 + 2}$$

A further approximation is made by employing determinations of μ made for wave-lengths of the visible region (which are relatively short waves). The results, however, are of considerable interest. Cuthbertson (*Phil. Mag.*, 21, 69, 1911) has recently determined ϵ for the rare gases, the values being as follows :—

He	Ne	Ar	Kr	Xe
$\epsilon = 0.04231$	0.04444	0.031848	0.032791	0.034545

These numbers show what a very small fraction of the total volume is actually occupied by the molecules themselves. If one knows the actual number of molecules in a given volume, it is easy to calculate the volume of each, and hence the diameter.

The most accurate method of determining the actual number of molecules in a given volume of a gas is the Einstein-Perrin method, which will be described in some detail later.

(2) Another method of calculating the diameter σ of a molecule is based upon the kinetic theory (see Meyer's *Kinetic Theory*, p. 300), and involves a knowledge of the mean free path λ , which can be obtained from viscosity measurement. The expression referred to is—

$$\frac{1}{\lambda} = \sqrt{2} \times n\pi\sigma^2$$

where n is the number of molecules in unit volume of the gas, and σ is the molecular diameter. The quantity ϵ , which is the actual volume of the molecules in unit volume of the gas, is given by the expression $\frac{4\pi n(\frac{\sigma}{2})^3}{3}$.

The results obtained with the help of Rankine's viscosity data (*Proc. Roy. Soc.*, **83**, 516, 1910) upon the rare gases are summarised in the following table (see Cuthbertson, *l.c.*):—

Gas.	Relative viscosity η .	Relative λ .	Relative σ .	Absolute radius of molecules.	ϵ (calculated).
He .	1'000	1'000	1'000	$0\cdot84 \times 10^{-8}$ cm.	0'04695
Ne .	1'585	0'704	1'19	$0\cdot9996 \times 10^{-8}$ „	0'031171
Ar. .	1'124	0'354	1'68	$1\cdot4112 \times 10^{-8}$ „	0'033296
Kr. .	1'253	0'274	1'91	$1\cdot6044 \times 10^{-8}$ „	0'034844
Xe. .	1'136	0'198	2'25	$1\cdot890 \times 10^{-8}$ „	0'037918

The value for the diameter of a molecule of these gases is approximately 2 to 3×10^{-8} cm.

It will be observed that the values of ϵ obtained from viscosity measurements agree reasonably well with those obtained by the refractive index method.

(3) Another method of determining the size of molecules depends on the application of the so-called "equation of state" of van der Waals. This equation is simply a modified form of the gas equation, $p v = RT$, when account is taken of the "lack of perfection" of actual gases owing to the presence of molecular attraction and the actual space taken up by the molecules themselves. The equation is considered at some length in Chap. II. For the present we shall simply assume its validity. The equation is usually written in the form—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

The term $\frac{a}{v^2}$ represents the correction term due to the molecular attractions, a being taken to be a constant and v the volume (of the gas or of the liquid). The term b is the limiting value which the volume v would assume under practically infinitely high pressure. It can be easily shown that if the molecules are spheres, and if, under the pressure referred to, the molecules actually touch one another, then the

volume term b will be $\frac{7}{6}$ of their actual volume.¹ If we are considering unit volume of the gas, that is $v = 1$, then $\frac{6}{7}b$ is simply ϵ . With the help of experimentally determined values of b it is therefore possible to determine the diameter of the molecules. The results obtained show that the order of magnitude is 10^{-8} cm.

(4) In 1858 Clausius put forward the following theorem : the ratio of the total space occupied by a gas to the actual volume of the molecules contained in the same space is equal to $\frac{8\lambda}{\sigma}$, where λ and σ have their usual significance. This was deduced prior to Maxwell's theorem of distribution of velocities among the molecules. On introducing the necessary correction, one obtains—

$$\frac{1}{\epsilon} = \frac{8.5\lambda}{\sigma}$$

Employing the values of ϵ and λ previously obtained, one can calculate σ . The following table contains a few of the results :—

Gas.	ϵ	σ .
Hydrogen	0.0333	4.7×10^{-8} cm.
Nitrogen	0.0387	6.7×10^{-8} „
Oxygen	0.0374	6.1×10^{-8} „
Carbon dioxide	0.0372	3.0×10^{-8} „

The values of σ obtained by this method are of the same order of magnitude as those given by other methods.

Values for σ have likewise been obtained from measurements of heat conduction and diffusion in gases. These are fully discussed in Jeans' *Dynamical Theory of Gases*. The

¹ Van der Waals has, however, shown that the b of his equation is four times the actual volume of the molecules. The apparent discrepancy comes in because if all the molecules were to touch one another simultaneously no kinetic movement would be possible, a state of affairs only realisable at absolute zero. This distinction, however, does not affect the order of magnitude of the quantity dealt with here.

results agree well with those obtained from viscosity measurements.

(5) Lord Rayleigh's surface tension method. Every liquid is characterised by the existence of a tension over its surface which acts as if the surface layer were an elastic film. This "surface tension" is very sensitive to the presence of impurities in the liquid. It was noticed long ago that if pieces of camphor be placed upon a water surface they move about rapidly, the motion being due to local alterations in the surface tension of the water surrounding the pieces of camphor. It was also observed that the camphor movements could be stopped by the addition of a very small trace of oil to the water surface. Lord Rayleigh estimated the minimal quantity of oil which had to be added to a known area of water to cause the movements just to cease. He thus found the "critical" thickness of the oil layer required. This was approximately 1.6×10^{-7} cm. Now, it cannot be assumed that the oil layer was just one molecule thick, but it cannot have been less than this, so that the above value represents a *major limit* of the molecular diameter. It is five to ten times that previously obtained.

(6) Among other methods which yield a major limit may be mentioned that of Oberbeck (*Wied. Ann.*, 31, 337, 1887), who found that a coating of metal 3×10^{-7} cm. in thickness was sufficient to alter the electrical potential of a platinum electrode (probably by the formation of an alloy on the surface). Further, Wiener found that a film of silver 2×10^{-8} cm. in thickness was sufficient to alter appreciably the phase of reflected light.

(7) The last method to be mentioned deals with the size of atoms (or molecules) of metals, and is due to Lord Kelvin (*Popular Lectures and Addresses*, vol. i. p 168). The principle of the method consists in measuring the amount of electrical work done in bringing two charged metal plates close to one another. If one brings two pieces of zinc and copper into contact at one corner they become electrified, and attract one another. Lord Kelvin calculated that when the air space between them is 10^{-5} cm. the attraction per unit

area is 2 grams' weight. One can imagine a pile of such plates built up with zinc and copper alternately, the air spaces being 10^{-5} cm., until the height of the pile is 2 cm. The electrical work done in the process of building up is 2 cm. grams. The whole mass of metal is 8 grams, and knowing the mean specific heat, it can be easily calculated that if this electrical work be converted into heat, the consequent rise in temperature would be $\frac{1}{16130}^{\circ}$ C. "Now let the thickness of each piece of metal and of each intervening space be 10^{-8} cm. The work would be increased one-million fold unless 10^{-8} cm. approaches the smallness of a molecule. The heat equivalent would therefore be enough to raise the temperature of the material 62° C." As this is barely possible from what we know of the heat of combination of zinc and copper in forming an alloy, it is reasonable to conclude that plates thinner than 10^{-8} cm. would be smaller than the atoms of the metals. It follows therefore that 10^{-8} cm. is the minimum admissible size of the atoms of copper and zinc, or what is the same thing, when these metals alloy, their atoms do not approach one another more closely than this. The method is, of course, very crude, but it is remarkable that we obtain once more a value of the same order of magnitude as that obtained in the case of gaseous substances.

THE MOST PROBABLE VALUES FOR THE MOLECULAR DIAMETERS OF SOME GASES (Sutherland, *Phil. Mag.*, **19**, 25, 1910).

Sutherland assumes that there are 2.77×10^{19} molecules of gas in 1 c.c. at normal temperature and pressure. This agrees well with Millikan's value (*Phil. Mag.*, **19**, 228, 1910), which will be considered later, namely, 2.76×10^{19} . Knowing the number of molecules per cubic centimetre, Sutherland recalculated the molecular diameters using the viscosity data given by Jeans. The following table contains the results;—

Gas.	Molecular diameter in cms. $\times 10^8$.	Gas.	Molecular diameter in cms. $\times 10^8$.
Hydrogen . . .	2.17	Oxygen . . .	2.71
Helium . . .	1.97	Argon . . .	2.66
Carbon monoxide .	2.74	Carbon dioxide .	2.90
Ethylene . . .	3.31	Nitrous oxide (N_2O)	3.33
Nitrogen . . .	2.95	Chlorine . . .	3.74
Air . . .	2.86		
Nitric oxide (NO) .	2.59		

§ 2

EVIDENCE FOR THE REAL EXISTENCE OF MOLECULES.

Hitherto we have found that the concept of molecules is a satisfactory working hypothesis by means of which the behaviour of gases (and to a less degree the behaviour of liquids) can be accounted for. No *direct* evidence, however, for the actual existence of very small discrete particles in rapid and continuous motion in a gas or liquid has yet been given. It is evident that if such can be given it places the kinetic theory upon a firmer basis. This is of special importance from the kinetic standpoint of physico-chemical processes. We shall therefore consider what evidence is available.

The Radiometer.—This instrument consists of a glass bulb, inside of which is pivoted a small paddle wheel with mica vanes, the vanes being blackened on one side. When the bulb is exhausted to a certain point, then on bringing a source of radiant heat near the vessel the paddle revolves, the unblackened sides of the vanes being foremost, *i.e.* in the direction of motion. This is explained as due to unequal bombardment of the sides of each vane by the molecules of the gas. The blackened side absorbs the radiant heat better than the unblackened, and hence the gas molecules in contact with the blackened side have imparted to them greater kinetic energy than those on the unblackened side. The molecules with greater kinetic energy strike the vane more vigorously than those on the unblackened side, and hence the vane is

subjected to a net pressure which causes it to move with the unblackened side foremost. This is fairly direct evidence for the actual existence of molecules. It must be pointed out, however, that the phenomenon is not so simple as the above account of it might lead one to imagine. If the bulb is not exhausted at all, the vanes remains stationary. If the exhaustion is only moderate, the direction of motion is actually the reverse of that described. This is explained by saying that at moderate pressures the mean free path of the molecules is so small and the number of collisions so great that the accelerated molecules which fly off from the blackened surface beat back the molecules with which they come in contact, and hence cause a local *rarefaction* of the gas on the blackened side, with the result that the vane moves with the blackened side foremost. As far as they go radiometer effects are fairly direct evidence for the existence of molecules. The first really conclusive evidence, however, has come from a quite unexpected source, namely, the phenomenon known as "Brownian Movement," exhibited by small particles suspended in liquids.

BROWNIAN MOVEMENT AND MOLECULAR REALITY.¹

If one examines with a microscope a liquid in which fine particles are suspended, such as an emulsion of mastix, or gamboge in water, or the still finer particles which are present in colloidal solutions of metals, hydroxides or sulphides (Chap. VIII), which can be rendered visible by means of the ultra-microscope, we find in all cases that the particles are in a state of rapid and irregular motion. This was first noticed in 1827 by the botanist Brown. The cause of these movements has naturally been the subject of much investigation, but it was not until 1879 that Ramsay (*Proc. Glasgow Phil. Soc.*) for the first time showed that they are very probably due to the bombardment of the particles by the molecules of

¹ See *Brownian Movement and Molecular Reality*, by J. Perrin, translated by F. Soddy (1910).

the liquid medium. In 1888 the French physical chemist Gouy independently arrived at the same conclusion. Gouy observed that the motion was not due to the light which necessarily passed through the liquid under examination, for he was able to reduce the intensity of the light to one-thousandth of its value without in the least affecting the movements. Neither is it due to convection currents in the liquid, for it persists after sufficient time has elapsed for thermal equilibrium to be established. Neither is it due to external vibration. Even the *nature* of the particles has very little influence upon the phenomenon, although their *size* is important, the smaller the particle the more vigorous the movement. The most remarkable feature is that the movement goes on *indefinitely*. No more satisfactory explanation has been put forward than that of Gouy, namely, that the movement is a direct consequence of the continuous irregular movements of the molecules of the medium. It serves therefore to visualise the movements of the molecules themselves. All this, however, is of a qualitative nature. We owe to Perrin the quantitative investigation of the phenomenon.

Assuming that the movement is due to molecular bombardment, Perrin sought to obtain, from measurements made upon the emulsion particles of mastix, rubber, and gamboge, values for what he calls the Avogadro Constant, namely, the actual number N of molecules in one grammole of a gas. N is known, at least roughly, from considerations with which we have already dealt in determining the size of the molecules. In the case of oxygen gas, for example, from the known value of ϵ one can calculate that N lies between 45×10^{22} and 200×10^{22} , the lower limit being probably the more correct. Also on the basis of the electromagnetic theory of radiation applied to the case of long (heat) waves, Lorentz has calculated¹ from Lummer and Pringsheim's data that $N = 77 \times 10^{22}$ (see Perrin, *l.c.*, pp. 88, 89).

Perrin's own method of investigation by means of the Brownian Movement may now be briefly outlined.

¹ An accurate determination of N can be obtained with the help of Planck's radiation equation (see Part III. (Vol. II.)).

It has been shown that in the case of a gas the pressure p is represented by the expression—

$$p = \frac{1}{3} \frac{nm}{v} u^2$$

where n is the number of molecules in v c.c.'s, and m the mass of a single molecule. Rewriting the above in the form—

$$pv = \frac{1}{3} nm u^2$$

and denoting by w the mean kinetic energy of each molecule ($w = \frac{1}{2} m u^2$), we obtain the alternative form—

$$pv = \frac{2}{3} n w$$

For a perfect gas the gas equation (with which the reader is assumed to be conversant) is $pv = RT$, in which R has the value 1.985 calories per degree or 83.2×10^6 c.g.s. units if the mass of gas considered be one grammole. Also, if we are considering one grammole, the number n can be written N , *i.e.* the number of molecules in one grammole of any gas. On combining the above two equations one obtains—

$$\frac{2}{3} N w = RT$$

or

$$w = \frac{3RT}{2N}$$

Hence, if we can measure w , the mean kinetic energy of a molecule, we can calculate N , for the other terms are known. Since the above relation applies to the gaseous state, one might be inclined to think that to obtain a value for w we would have to confine ourselves to the gaseous state. This, however, is not necessary provided we assume the validity of the important generalisation known as the Law of Equipartition of Energy among the various particles constituting a system. By applying this principle it is possible to calculate w from the Brownian movement of particles suspended in *liquids* and hence obtain a value for N . What is meant by the equipartition of energy as applied to this case may be most briefly given in Perrin's own words (Perrin, *l.c.*, pp. 18, 19):

"We have seen that the mean molecular energy is, at the same temperature, the same for all gases. This result remains

valid when the gases are mixed. . . . For example, the molecules of carbon dioxide and water vapour, present in the air, must have the same mean kinetic energy in spite of the difference in their natures and masses. This invariability of molecular [kinetic] energy is not confined to the gaseous state, and the beautiful work of van 't Hoff¹ has established that it extends to the molecules of all dilute solutions. Let us imagine that a dilute solution is contained in a semi-permeable enclosure which separates it (the solution) from the pure solvent. We suppose this enclosure allows free passage to the molecules of the *solvent*, in consequence of which these molecules cannot develop any pressure, but that it stops the *dissolved* molecules. The impacts of these molecules against the enclosure will then develop an *osmotic* pressure P , and it is seen if the reasoning is considered in detail, that the pressure produced by these impacts can be calculated as in the case of a gas, so that in consequence we write $Pv = \frac{2}{3}nW$, W signifying the mean kinetic energy of translation of each of the n molecules [of dissolved substance or 'solute'] contained in the volume v of the enclosure. Now van 't Hoff has observed that the experiments of Pfeffer give for the osmotic pressure the same value as that which would be exerted by the same mass of dissolved substance if it alone occupied in the *gaseous* state the volume of the enclosure. W is thus equal to w ; the molecules of a dissolved substance have the same mean kinetic energy as in the gaseous state [at the same temperature]. . . . van't Hoff's law tells us that a molecule of ethyl alcohol in solution in water has the same [kinetic] energy as one of the molecules of vapour over the solution. It would still have the same energy if it (the ethyl alcohol molecule) were present in chloroform (that is to say if it were surrounded by chloroform molecules) or even if it were in methyl or propyl alcohols. This indifference to the nature of the molecules of the liquid in which it moves makes it almost impossible to believe that it would not still have the same energy if it (the ethyl alcohol molecule) were in ethyl alcohol; that is, if it forms one of the molecules of pure ethyl alcohol. It therefore follows that

¹ Chapter IV.

the [kinetic] molecular energy is the same in a liquid as in a gas [at the same temperature], and we can now say :

“At the same temperature all the molecules of all fluids have the same mean kinetic energy which is proportional to the absolute temperature.”

“But this proposition, already so general, can be still further enlarged. According to what we have just seen, the heavy molecules of sugar,¹ which move in an aqueous sugar solution, have the same mean kinetic energy as the lighter molecules of water. These sugar molecules contain 35 atoms; the molecules of sulphate of quinine contain more than 100 atoms, and the most complicated and heaviest molecules to which the laws of van 't Hoff can be extended may be cited. The applicability of the generalisation [of the equipartition of kinetic energy] does not appear to be limited to any *size* of molecule. Let us now consider a particle a little larger still, itself formed of several molecules, in a word, a speck of dust. Will it proceed to react towards the impacts of the molecules encompassing it according to a new law? Will it not comport itself simply as a very large molecule, in the sense that its mean kinetic energy has still the same value as that of an isolated molecule? This cannot be averred without hesitation, but the hypothesis at least is sufficiently plausible to make it worth while to discuss its consequences. Here we are then taken back again to the observation of the particles of an emulsion, and to the study of this wonderful movement which most directly suggests the molecular hypothesis. But at the same time we are led to render the theory precise by saying, not only that each particle owes its movement to the impacts of the molecules of the liquid, but further that the energy maintained by the impacts is on the average equal to that of any one of these molecules. . . . So that if we find a means of calculating this granular energy [*i.e.* the kinetic energy of the particles or granules] in terms of measurable magnitudes, we shall have at the same time a means of proving our theory.”

¹ Pfeffer's experiments were carried out with solutions of cane sugar, and van 't Hoff showed that the osmotic pressure of dissolved sugar molecules obeyed the gas law, $pv = RT$.

PERRIN'S FIRST METHOD.

This method consisted in determining the distribution of the emulsion particles under the action of gravity. Just as air is densest at the surface of the earth, so an emulsion distributes itself in such a way that the lower layers have a higher concentration of granules than the upper layers. Let us imagine an emulsion filling a vertical cylinder of cross-sectional area s square cm. Consider a horizontal slice of the emulsion at a height h from the base. Suppose that at this level the number of granules is n *per unit volume*. Similarly, at a height $h + dh$ the number of granules per unit volume is $n - dn$ (as h increases the concentration of the granules decreases, hence the negative sign). The osmotic pressure of the granules at the height h is $\frac{2}{3}nW$, where W is the mean kinetic energy of each granule. At the height $h + dh$ the osmotic pressure is $\frac{2}{3}(n - dn)W$. The difference of osmotic pressure which exists between the two planes is $-\frac{2}{3}dnW$. Now pressure denotes force per unit area, and hence the difference of the osmotic forces acting over the area s is $-\frac{2}{3}sdnW$. But the granules as a whole are in equilibrium, and therefore this difference of osmotic forces between the two planes must be balanced by the difference of the gravitational attractions exerted at the two planes. If ϕ is the volume of a single granule, D its density, δ the density of the liquid medium, and g the acceleration of gravity, then the effective weight or downward force exerted upon a single granule is $\phi(D - \delta)g$. The volume of liquid between the two planes considered is sdh , and if there are n granules per unit volume (more strictly $\frac{2n + dn}{2}$), the total gravitational pull upon all the granules present between the two planes is—

$$nsdh\phi(D - \delta)g$$

It is this force which prevents the granules distributing themselves at the same concentration throughout the entire liquid between the two planes, and therefore it is this force which opposes and balances the osmotic force $-\frac{2}{3}sdnW$. Equating these two forces, we obtain—

$$-\frac{2}{3}sWdn = nsdh\phi(D - \delta)g$$

We can integrate this expression so that it gives a relation between n_0 and n , the number of granules per unit volume or concentration of granules at two planes separated by a finite distance h . The resulting expression is—

$$\frac{2}{3}W \log \frac{n_0}{n} = \phi(D - \delta)gh$$

Further, since W is identical with w , the mean molecular kinetic energy, W may be written $\frac{3}{2} \frac{RT}{N}$, and hence the above expression may be transformed into—

$$2.303 \frac{RT}{N} \log_{10} \frac{n_0}{n} = \frac{4}{3} \pi r^3 g (D - \delta) h \quad . \quad (5)$$

where 2.303 is the factor which reduces natural to common logs, and r is the radius of a granule.

It follows, therefore; that if we can measure the number of granules present at various heights in an emulsion and apply the above equation, we can calculate N , the "Avogadro Constant." Perrin employed emulsions of gamboge, mastix, and rubber latex. The emulsion granules were made uniform in size by centrifuging. The density D of the granules was obtained, first, by measuring the density of the substance in the massive or "solid" form, and, secondly, by determining the actual density of an emulsion, evaporating to dryness and weighing the quantity of gamboge, etc. The results of the two methods were concordant. The measurements of h and n were carried out within the limits of a microscope slide, having a small cavity, such as is used for counting the number of blood corpuscles. The microscope (Fig. 3) was focussed

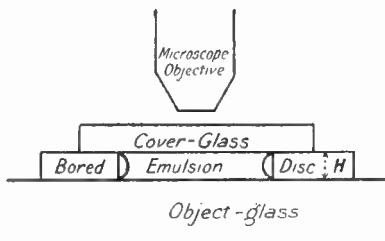


FIG. 3.

at different depths of the emulsion, and the average number of particles in the field of view at each level noted. By

carrying out an immense number of determinations Perrin succeeded in determining n and h very accurately. For details the monograph already cited should be consulted. The only other quantity to be mentioned is the size of the granules. The first method employed by Perrin is simply the method of Sir J. J. Thomson for counting the number of electrically charged particles in an ionised gas, namely, by observing the rate of fall of a cloud of particles under the action of gravity. Stokes has shown that when a particle moving at a steady rate through a medium of viscosity η encounters a frictional resistance the magnitude of the force causing the motion is given by the expression $6\pi\eta rv$, where r is the radius of the particle (assumed to be large compared with the molecular structure of the medium through which the particle passes), and v is the steady rate of motion. If gravity is the cause of the motion, the gravitational force acting on a falling granule is $\frac{4}{3}\pi r^3(D - \delta)g$, and we can equate the two expressions—¹

$$6\pi\eta rv = \frac{4}{3}\pi r^3(D - \delta)g$$

from which r can be calculated.

Perrin used a capillary tube (so as to avoid convection currents), and after shaking the emulsion so that it was at uniform concentration throughout, the rate was observed at which the emulsion cleared at the top; that is, the rate of descent of the upper layers, which of course at this stage were not in the equilibrium state of distribution previously considered in the deduction of the expression for N . The only doubtful point is whether Stokes' Law holds for particles as small as these granules, the diameter of which is approximately 2×10^{-5} cm. As a matter of fact, as will be shown later in connection with Millikan's determination of the charge on an electron, Stokes' Law is nearly but not quite correct. The agreement obtained, however, between the method just described and a modification about to be mentioned affords confirmation of the general validity of the Stokes expression

¹ In this connection, see Einstein's treatment of movement of particles in a viscous medium given on p. 31.

even for particles of these dimensions. The modification depends on the observation that if the liquid be made first faintly acid, then, when a granule comes near the wall of the

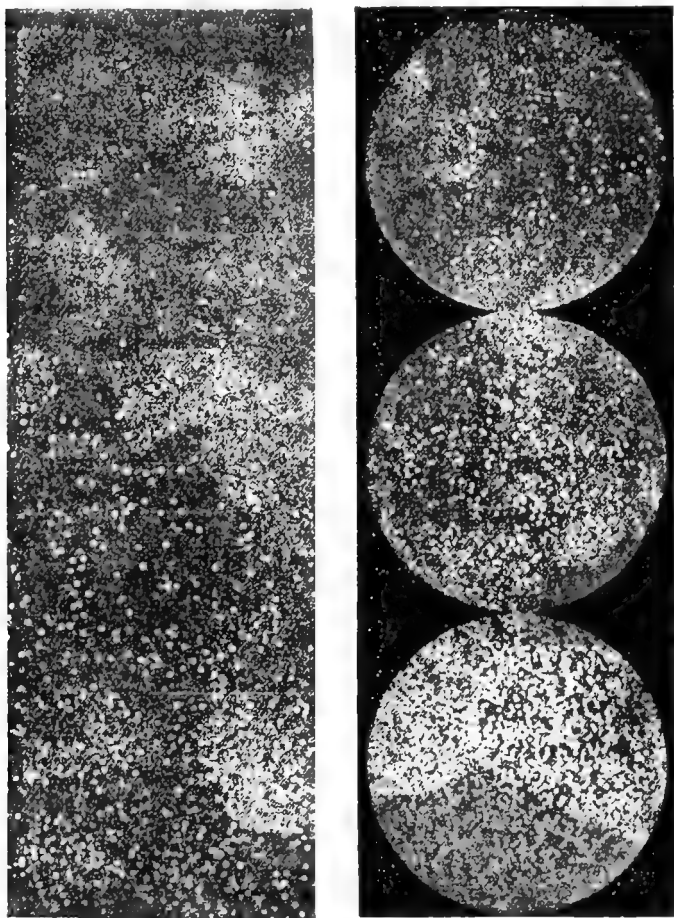


FIG. 4.

cell it sticks, although the granules in the bulk of the liquid are still in rapid motion. By this means it is possible to remove all the granules from solution and count them, thereby allowing a calculation to be made of the *average* number of

granules per cubic centimetre throughout the emulsion. If the total mass of gamboge is known, it is easy to calculate the volume of each granule, and therefore the radius, r .

Perrin carried out five series of experiments with gamboge emulsions, each experiment necessitating the counting of several thousand granules. The mean value for N obtained by the aid of the equation (5) was 69×10^{22} , a number which agrees sufficiently closely with the approximate values of N already referred to to justify the conclusions of Gouy regarding the cause of Brownian movement. With mastix emulsions Perrin found $N = 70.0 \times 10^{22}$, and finally, as a result of further series of experiments with gamboge carried out with great care, Perrin obtained the value 70.5×10^{22} .

PERRIN'S SECOND METHOD.

This method is based upon theoretical considerations first put forward by A. Einstein (*Ann. der Physik.*, [4] 17, 549, 1905; *ibid.*, [4] 19, 371, 1906). Einstein does not consider the concentration distribution of granules in different layers, but fixes attention upon the trajectory of a single granule along one axis—say the x axis—in one plane (xy). The actual path traversed would be quite impossible to follow, and therefore Einstein considers only the mean *rectilinear* displacement during a given time, the displacement being defined as the length of the straight line *measured as along the x axis*, which joins the point of departure to the point of arrival. In actual observations—taking a time interval of, say, 30 seconds—the displacements vary considerably from one another, but by taking a sufficient number of observations it is possible to estimate the *mean displacement* Δ with considerable accuracy. As Perrin succeeded in determining N by this means with even greater accuracy than by the first method, it is of interest to follow Einstein's mode of treatment. In the following it is given practically in Einstein's own words.¹

¹ The section which follows is a translation (with certain changes) of a paper by Einstein in the *Zeitsch. für Elektrochem.*, 14, 235-239, 1908, entitled "Elementary Theory of the Brownian Movement." The more rigid mathematical treatment is given in the *Annalen* papers referred to,

EINSTEIN'S THEORY OF DIFFUSION AS APPLIED TO BROWNIAN MOVEMENT.

Diffusion and Osmotic Pressure.—Suppose the cylindrical vessel z filled with a dilute solution (Fig. 5). The internal space is divided into two parts by means of a semi-permeable movable piston, the piston being entirely permeable to the solvent but impermeable to the solute. If the concentra-

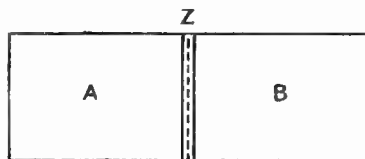


FIG. 5.

tion of solute in A is greater than that in B, there will be a force exerted upon the piston tending to move it towards the right. This force, reckoned per unit area of the piston, will be denoted by K . K evidently is the difference of the osmotic pressures exerted by the solute on the two sides of the piston. If no external force be applied, the piston will move towards the right until the concentrations in both compartments become identical. It follows therefore that osmotic pressure is the agency causing diffusion until equi-concentration is reached; for we can prevent this state being reached by balancing the osmotic pressure difference K by means of an external force applied to the piston. Suppose now that there is no piston in the cylinder, but that the concentration on the left-hand side is greater than on the right, then diffusion of the solute will take place from left to right. Consider the case depicted in Fig. 6.

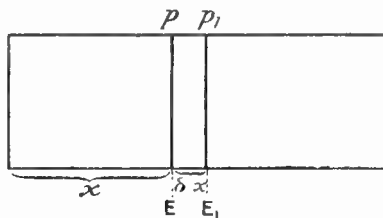


FIG. 6.

From the left the osmotic pressure p acts on the surface E , on the right the pressure p_1 acts on the surface E_1 . The resulting pressure is $p - p_1$. Let x be the distance of E from the left-hand end of the cylinder, $x + \delta x$ the distance of E_1 from the same end, the distance between E and E_1 being δx . Since $p - p_1$ is the osmotic

pressure which acts on the volume δx occupied by the solute, it follows that the osmotic pressure difference reckoned per *unit* volume is

$$\frac{p - p_1}{\delta x} = -\frac{p_1 - p}{\delta x} = -\frac{dp}{dx}$$

which we shall represent by the symbol K_0 . Since further the osmotic pressure is given by the equation—

$$p = RT\nu$$

where R is the gas constant (8.31×10^7 c.g.s. units), T the absolute temperature, and ν the number of grammoles of solute per unit volume of solution in the region E , we obtain for the osmotic pressure difference reckoned per unit volume the expression—

$$K_0 = -RT \frac{d\nu}{dx} \quad . \quad . \quad . \quad . \quad (6)$$

In order to calculate the *rate* of diffusion, one must know how great is the resistance offered by the solvent to the diffusion process. If in general a driving force k acts on a molecule, the resulting velocity v will be given by the equation—

$$v = \frac{k}{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where C is a constant which we might call the frictional resistance of the molecule. If we assume that a dissolved molecule is spherical, and likewise large compared to a molecule of solvent, then we have the expression $C = 6\pi\eta r$ (Stokes' Law), where η is the viscosity of the solvent and r the radius of the molecule of the solute. It may be observed that the assumption made regarding the relative size of solute and solvent molecules would be in all probability incorrect in the case of "true" solutions. In the case of emulsions and colloidal solutions, however, the work of Perrin has shown that the expression holds fairly well. It will be observed that we are making no sharp distinction between pseudo-solutions, *i.e.* emulsions and colloids, and "true" solutions.

We can now calculate the quantity of solute which diffuses

through unit cross-sectional area of the cylinder in unit time. In the unit volume there are ν grammoles, that is, νN actual molecules, if N is the actual number of molecules in one gram-mole of gas or dissolved substance. If, therefore, K_0 divides itself over these νN molecules contained in unit volume, it follows that K_0 will give to these a velocity which would be the $\frac{1}{\nu N}$ th part of that which it would give to a single molecule if it were exerted on this alone. One obtains, therefore, from equation (7) for the velocity which the force K_0 can impress on νN particles the expression—

$$v = \frac{1}{\nu N} \cdot \frac{K_0}{C}$$

In the case which we have been considering K_0 represents difference of osmotic pressure reckoned per unit volume, so that on introducing equation (6) one obtains—

$$\nu v = - \frac{RT}{N} \cdot \frac{1}{C} \cdot \frac{dv}{dx}$$

On the left-hand side stands the product of the concentration ν of the solute and the velocity with which the solute moves in the diffusion process. This product represents, therefore, the quantity of solute transported per second by diffusion through the unit cross-sectional area. This quantity divided by $-\frac{dv}{dx}$ is the diffusion coefficient D , when we define D as the quantity of solute transported per second through a unit cube when the concentration difference between the two ends of the cube is unity. Thus one obtains the relation—

$$D = \frac{RT}{N} \cdot \frac{1}{C} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In the special case in which the diffusing molecules are large compared with the molecules of the solvent, we can substitute Stokes' value for C , and write—

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

DIFFUSION AND IRREGULAR MOVEMENTS OF MOLECULES.

The molecular theory of heat opens up a second point of view from which the process of diffusion can be considered. The irregular movements which are due to the heat content of a substance will be such that a single molecule of a gas or liquid will move about absolutely irregularly. The result of this movement in the case of dissolved molecules will be that any concentration differences initially existing in different parts of the solution will gradually vanish. Let us consider this process somewhat more closely, making the same assumptions as in the foregoing paragraphs, namely that we restrict ourselves to the diffusion in the direction of the x axis of the cylinder. We shall consider that at a given moment t we know the x co-ordinates of all the dissolved molecules and likewise at a time $t + \tau$, where τ denotes such a short interval of time that the concentration (or rather the distribution) relations of the molecules in the solution have only altered to a slight extent. During this time τ the x co-ordinate of the first dissolved molecule will alter by a given quantity Δ_1 , due to the irregular heat movements, the second molecule's co-ordinate will alter by an amount Δ_2 , and so on. These displacements Δ_1 , Δ_2 , etc., will be partly negative (to the left), partly positive (to the right). Further, the extent of these displacements for the same molecule will vary much. But since we are considering a dilute solution, the displacements (of a solute molecule) are due to the surrounding solvent, not to any appreciable extent to the other solute molecules, and therefore the mean displacement Δ in differently concentrated solutions will be the same, and will be as often positive as negative. We have now to find out how much solute will diffuse in time τ through unit cross-sectional area when the mean magnitude Δ of the displacements is known in the direction of the x axis. To simplify the matter, the calculation will be carried out as if all the molecules experienced equal displacements Δ , one half being positive (to the right) and one half negative (to the left). Consider the state of

things represented by Fig. 7. Through the plane E of a cylinder of unit sectional area during the time τ only those solute molecules will pass from left to right which initially occupied positions less distant from E than the range Δ . These molecules lie between Q_1 and E. But of these molecules only one-half have *positive* displacement, so that only one-half of them pass through the plane E. This number is $\frac{1}{2}\nu_1\Delta$, where ν_1 is the mean concentration (number per unit volume), that is, the concentration at the medium plane M_1 . Since the sectional area is unity, Δ represents the volume Q_1E .

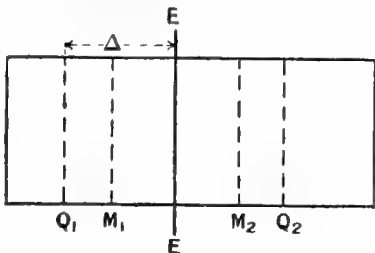


FIG. 7.

Analogous reasoning in the case of motion from right to left gives the expression $\frac{1}{2}\nu_2\Delta$, where ν_2 is the concentration at the plane M_2 . The net quantity of solute which diffuses from left to right in the time τ is the difference of the two expressions, namely $\frac{1}{2}\Delta(\nu_1 - \nu_2)$.

ν_1 and ν_2 represent the concentrations at two planes which are separated from one another by the small quantity Δ . If one denotes by x the distance of any plane from the left-hand end of the cylinder, then we can write—

$$\frac{\nu_2 - \nu_1}{\Delta} = \frac{d\nu}{dx} \quad \text{or} \quad \nu_1 - \nu_2 = -\Delta \frac{d\nu}{dx}$$

so that the quantity of solute diffused through E in time τ is

$$-\frac{1}{2}\Delta^2 \frac{d\nu}{dx} \dots \dots \dots (9)$$

The quantity in grammoles which diffuses in unit of time under the concentration gradient $\frac{d\nu}{dx}$ is therefore—

$$-\frac{1}{2} \cdot \frac{\Delta^2}{\tau} \cdot \frac{d\nu}{dx}$$

Hence the quantity which would diffuse under unit concentration gradient (that is, when the concentrations at two different points unit distance apart differ by unity) is—

$$-\frac{\frac{1}{2} \cdot \frac{\Delta^2}{\tau} \cdot \frac{dv}{dx}}{\frac{dv}{dx}} \quad \text{or} \quad -\frac{1}{2} \cdot \frac{\Delta^2}{\tau}$$

But this is simply the diffusion coefficient D .

Hence
$$D = -\frac{1}{2} \cdot \frac{\Delta^2}{\tau} \quad . \quad . \quad . \quad . \quad (10)$$

where Δ is the mean displacement¹ of any molecule along the x axis.

THE DISPLACEMENT OF SINGLE MOLECULES.

If one combines equations (8) and (10), one obtains the relation—

$$\Delta = \sqrt{\frac{2RT}{NC}} \times \tau$$

From this formula we see that the mean displacement of a single molecule along one axis is not proportional to the time, but to the square root of the time. This arises from the fact that in two consecutive time units the distances traversed are sometimes positive, sometimes negative. In the case in which the dissolved molecule is large compared with the molecules of the solvent, and is likewise spherical, we can use equation (8a) in place of (8), and thus obtain the relation—

$$\Delta^2 = \tau \cdot \frac{RT}{N} \cdot \frac{1}{3\pi\eta r}$$

This is the equation employed by Perrin in his second method of investigating the Brownian Movement, which will now be briefly described. Perrin used as before emulsions of gamboge and mastix.

¹ More accurately, Δ should be taken to be the root-mean-square displacement.

In the accompanying diagram (Fig. 8) are reproduced three typical drawings of the path traced out by a mastix granule, the time intervals between each dot being 30 seconds. It is necessary to be quite clear as to how Δ^2 , the mean-square-displacement of a particle along a given axis, is

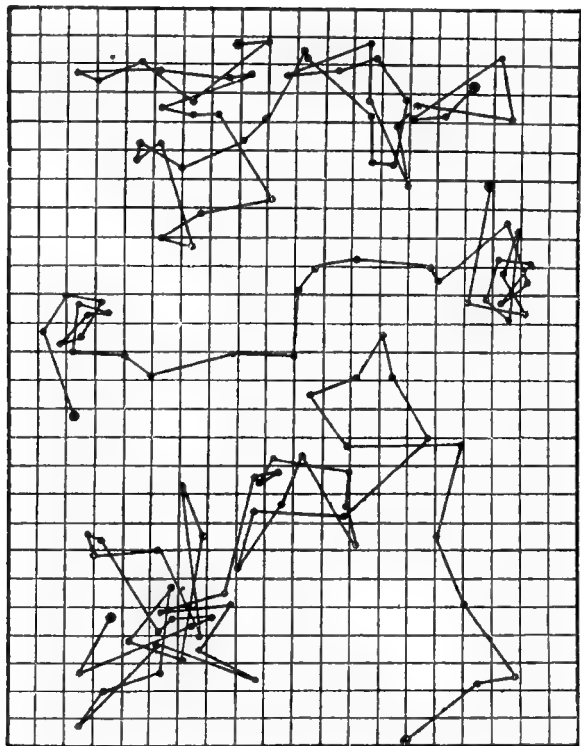


FIG. 8.

obtained from the observed path traced out. Suppose that L (Fig. 9) denotes the linear distance traversed in any 30 seconds interval in the plane to which the microscope is focussed. Then $L^2 = x^2 + y^2$, and adding up numerous intervals, $\Sigma L^2 = \Sigma x^2 + \Sigma y^2$. But since the direction of the paths is quite irregular, if sufficient readings are taken, the sum

of all the distances travelled by the particle along the x axis is equal to the sum along the y axis; that is $\Sigma x^2 = \Sigma y^2$, and therefore

$$\Sigma x^2 = \frac{1}{2} \Sigma L^2$$

Now the mean-square-displacement Δ^2 is simply the mean of the terms denoted by Σx^2 , and therefore Δ^2 is one-half of the mean square of the observed paths (L) in the horizontal plane xy .

Perrin observed several thousands of such displacements with gamboge and mastix granules, and after applying Einstein's equation, he obtained as a mean result—

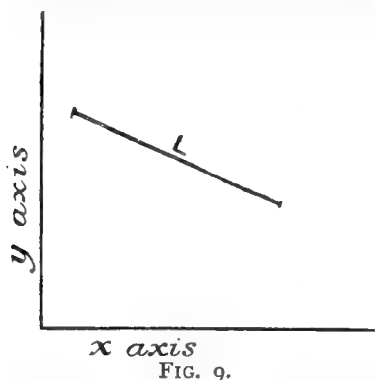
$$N = 71.5 \times 10^{22}$$

which agrees extremely well with the values obtained by the first method.¹ Recently Perrin (*Comptes Rendus*, 152, 1380, 1911) has repeated his experiments, using resin emulsions. The method of measuring the equilibrium concentration distribution at different levels led to the value 68.3×10^{22} . The method depending upon Einstein's equation led to the value 68.6×10^{22} . The most accurate mean value up to the present is, according to Perrin—

$$N = 68.5 \times 10^{22}$$

Reference will be made later to other determinations of N in discussing the question of the charge on an electron.

¹ Perrin also verified another equation deduced by Einstein involving a measurement of the *rotation* of the granules, but as this is much more difficult to observe, the results are presumably less accurate.



SVEDBERG'S INVESTIGATIONS UPON THE APPLICABILITY OF BOYLE'S LAW TO COLLOIDAL SOLUTIONS. (See *Zeitschr. physik. Chem.*, **73**, 547, 1910; *ibid.*, **77**, 145, 1911.)

The work carried out within recent years by Theodor Svedberg in connection with the osmotic pressure of colloidal solutions,¹ is based on certain relationships deduced by von Schmoluchowski (Boltzmann Festschrift, *Annalen der Physik*, p. 626, 1904; *ibid.*, [4] **25**, 205, 1908), in which the compressibility β_0 of a perfect gas is connected with the compressibility β of a non-perfect gas in terms which are measurable in the case of a colloidal solution, the latter being at first sight a very extreme case indeed of a non-perfect gas.

Svedberg determined the ratio $\frac{\beta}{\beta_0}$. If the gas law applied accurately to the particles of a colloidal solution, the ratio should be unity. Working with dilute colloidal solutions Svedberg obtained for the ratio a mean value very nearly unity, a few of the actual values (chosen practically at random), being 0.903, 0.981, 0.988, 1.00, 1.013, 1.029. These results support in a very conclusive manner the kinetic treatment of the behaviour of particles in colloidal solution.

THE MEAN KINETIC ENERGY OF A MOLECULE AT 0° C.

In the account of Perrin's determination of N we saw that the mean kinetic energy w of a molecule was given by the expression—

$$w = \frac{3}{2} \cdot \frac{RT}{N}$$

Setting $R = 83.2 \times 10^6$ c. g. s. units, and employing Perrin's value for N , it is easy to calculate w for $T = 273^\circ$. The result is 4.89×10^{-14} ergs, or 1.14×10^{-21} calories. This is the mean kinetic energy of a molecule at 0° C., and is independent of the physical or chemical state of the system considered,

¹ Colloidal solutions are discussed in Part I., Chap. VIII.

i.e. it holds equally for the molecules of *any* substance, whether solid, liquid, or gaseous.

NOTE.—As regards the question of movement of molecules in solids, see, however, Part III. (Vol. II.).

THE ELECTRICAL CHARGE ON A MONOVALENT ELECTROLYTIC ION.

It is known that one faraday of electricity, or 96,540 coulombs, is required for the deposition from solution of one gram equivalent of any ion (or charged atom). If we have a solution containing one grammole of hydrochloric acid and electrolyse it completely, evidently the number of hydrogen ions discharged at the cathode will be identical with the number of molecules of hydrochloric acid originally present in the solution,¹ that is, 68.5×10^{22} . Hence the charge on a

single hydrogen ion is $\frac{96540}{68.5 \times 10^{22}}$ coulombs, or 4.19×10^{-10} electrostatic units. [One coulomb is $\frac{1}{10}$ of one electromagnetic unit, and one electromagnetic unit is 3×10^{10} electrostatic units.]

We shall see later that the charge on a monovalent electrolytic ion is identical with that on an electron—that is, identical in magnitude though not necessarily in sign, since electrons are negatively charged, while cations are positively charged, and anions negatively.

§ 3

THE CONSTITUTION OF MOLECULES AND ATOMS.

We can obtain some information of a more or less qualitative nature respecting the differences in constitution of the molecules of various gases from considerations of the specific heat of the gas. A gas possesses two specific heats: first, the specific heat at constant volume, denoted by C_v , which represents the amount of heat which has to be added to one gram

¹ Reckoned, of course, as though there had been *no* electrolytic dissociation of the HCl to start with.

of the gas to raise its temperature one degree, the volume of the gas being kept constant; and secondly, the specific heat at constant pressure, denoted by the symbol C_p , which represents the amount of heat required to raise one gram one degree, the volume being allowed to expand at constant pressure. In the latter case the gas does *work* against the atmosphere, the amount of such work being represented by the product of the pressure into the increase in volume. As we shall see in dealing with the principles of thermodynamics (Part II., Chap. I. (Vol. II.)), this work must be done at the expense of some of the heat added, and therefore it requires more heat to be added to raise the temperature of the gas at constant pressure than it does at constant volume. We have now to find an expression for the difference of the two specific heats; that is, the heat equivalent of the work done by expansion. Consider one gram of gas at volume v , temperature T , and pressure p . The relation between these quantities is $p v = R T$, where R has in this instance the numerical value $\frac{1.985 \text{ calories}}{\text{molecular weight of the gas}}$.

Again consider the same mass of gas at the temperature $(T + 1)$, the pressure being p as before, but the volume is now greater, namely, v_1 . Again the relation $p v_1 = R(T + 1)$ must hold. Subtracting the two equations one finds $p(v_1 - v) = R$. But $p(v_1 - v)$ is the work done¹ in the expansion at constant pressure during the heating-up process. Hence the work done is R heat units, and this must be the difference of the two specific heats, that is—

$$C_p - C_v = R$$

Hence the gas equation can be written in general—

$$p v = (C_p - C_v) T$$

Also, we saw on the basis of the kinetic theory that—

$$p v = \frac{1}{3} n^2 \quad (\text{for a mass of 1 gram})$$

and therefore $n^2 = 3(C_p - C_v) T$

Further, since the expression for the kinetic energy of translation of a molecule is $\frac{1}{2} m u^2$, it follows that the total kinetic

¹ See Part II., Chap. I. (Vol. II.).

energy of translation of one gram is $\frac{1}{2}u^2$. Besides this energy of translation there is also internal energy in the molecules themselves due to internal vibrations, rotations of atoms round one another, etc. Let us make the assumption¹ that this internal energy is proportional to the energy of translation, that is, is given by the expression $K\frac{1}{2}u^2$, where K is a constant. Hence the total energy of all sorts in one gram of gas at a temperature T is—

$$\frac{1}{2}(1 + K)u^2$$

which is equal to—

$$\frac{3}{2}(C_p - C_v)(1 + K)T$$

Now if heat be added to the gas so as to raise its temperature one degree, the volume being kept constant, *i.e.* no external work being done, then all the heat added goes to increase the energy of the molecules. This increase is simply the specific heat at constant volume C_v , and is likewise the difference between the total energy at $(T + 1)$ and the total energy at T . That is—

$$\begin{aligned} C_v &= \frac{3}{2}(C_p - C_v)(1 + K)(T + 1) - \frac{3}{2}(C_p - C_v)(1 + K)T \\ &= \frac{3}{2}(C_p - C_v)(1 + K) \end{aligned}$$

Further, if we put the ratio $\frac{C_p}{C_v}$ equal to γ , then the above equation may be transformed into—

$$\gamma = 1 + \frac{2}{3(1 + K)}$$

Since we may expect K to be *in general* a positive quantity, this relation shows that—

$$\gamma > 1\frac{2}{3} \text{ or } 1.666$$

In the particular case of monatomic gases (the rare gases and metallic vapours) the internal rotation of atoms with

¹ This is simply an attempt to avoid introducing at this stage the Boltzmann theory of the equi-partition of energy among the different “degrees of freedom” of the molecule. This is discussed a little later and more fully in Part III. (Vol. II.).

respect to one another is impossible, so that putting $K = 0$ we obtain for this case—

$$\gamma = 1.666$$

These conclusions may be tested by direct measurements of specific heats, from which one obtains values for γ . In the following table the values for γ for a few gases are given:—

	γ
Mercury vapour, Hg	1.666
Nitrogen, N_2	1.410
Ammonia, NH_3	1.30
Methyl ether, $(CH_3)_2O$	1.113
Ethyl ether, $(C_2H_5)_2O$	1.029 ¹

With increasing complexity of the molecule K necessarily increases in magnitude, with the result that γ decreases.

We cannot learn more about molecular constitution from the study of specific heats unless we introduce the principles which belong to “statistical mechanics” (*cf.* Part III. (Vol. II.)). We shall here only indicate the meaning of the term “degrees of freedom” of a molecule.

A degree of freedom is defined as an independent mode in which a body may be displaced. To find out the number of degrees of freedom possessed by a body or system let us consider a simple case, namely, a single rigid body in space, say a solid sphere. The centre of gravity of the body is free to move parallel to any of the three space co-ordinates X, Y, Z . That is to say, as far as *translation* is concerned, a body, free to move in space, possesses *three* degrees of freedom. But such a body is likewise capable of *rotation*. It may rotate about three axes parallel to XYZ . (All other rotations can be resolved into component rotations about each of these three axes.) On the whole, therefore, a body such as we have been considering possesses *six* degrees of freedom. If a body possesses a “constitution” of some kind, that is, is made up of

¹ Ether has been investigated in a very complete manner by Perman, Ramsay, and Rose-Innes (*Zeitschr. physik. Chem.*, **23**, 385, 1897), values of γ being directly calculable from the observed velocity of sound measured both for the vapour and liquid over a wide temperature and pressure range.

various portions, each of which may rotate or vibrate with respect to one another, the number of degrees of freedom of the body is correspondingly increased, and to estimate the actual number of degrees of freedom soon becomes impossible. The important generalisation connected with degrees of freedom, and known as Boltzmann's "theorem of the equipartition of energy" between the different degrees of freedom possessed by a body may be stated thus: The total kinetic energy of a system (due to translation, rotation, vibration, etc.) is *equally* divided up between all the degrees of freedom, and it can be shown that the amount of energy per degree of freedom amounts to $\frac{1}{2}RT$, the unit of mass being the gram-mole. This theorem has been much criticised, but it would be altogether beyond our purpose to attempt to follow it. The application of the theorem in connection with the heat content of solids is discussed in Part III. (Vol. II.).

Although we have not been able to infer much regarding constitution from specific heat, a more successful attack has been made upon the problem from the standpoint of "electrons" or "corpuscles," of which, according to Sir J. J. Thomson, electricity—negative electricity—itself consists.

§ 4

SOME APPLICATIONS OF THE CORPUSCULAR OR ELECTRON THEORY TO THE PROBLEM OF MOLECULAR AND ATOMIC CONSTITUTION.

According to this theory, negative electricity consists of extremely small particles called corpuscles or electrons, which are all identical in size, and carry the same charge. These corpuscles are much smaller than atoms, and according to the theory, atoms, and therefore molecules, are partly built up of corpuscles. Of course to prevent spontaneous disintegration of the atom due to the mutual repulsion of a number of similarly charged electrons, it is necessary to assume the existence of an equal amount of positive electricity. It is assumed, therefore, that a neutral atom consists of a sphere of positive

electricity (J. J. Thomson) which contains a number of corpuscles moving in various orbits, the number of such corpuscles and the kind of motion they possess being the ultimate source of chemical and physical "properties." It will be of interest to consider briefly the experimental evidence in favour of the real existence of corpuscles.

Corpuscles were first discovered during the electrical discharge through a highly exhausted tube. Rays are shot off from the cathode, and these may be stopped by the interposition of some material placed in their path. These cathode rays, as they are called, on striking the walls of the tube cause a vivid green fluorescence upon soda glass, blue on potash glass. That these rays consist of negatively charged particles was shown by the fact that they can be deflected in certain directions by a magnetic or an electrostatic field, or both simultaneously. The first important quantity which would serve to characterise these rays is the ratio of their mass to their charge. To obtain this we have to consider the effects produced by a magnetic and an electrostatic field upon the direction of motion of the particles. Suppose that a single corpuscle mass m carrying a charge e is moving with a velocity v cms. per second through the tube, then by putting on a magnetic field of strength H it is possible to deflect the course of the corpuscle in a given direction. If simultaneously an electrostatic field be set up (by connecting two parallel pieces of metal placed inside the tube to the two ends of a battery) in such a direction that it just compensates the effect of the magnetic field so that the path of the corpuscle is undeflected, then we can equate the effect due to the magnetic field to that due to the electrostatic. The magnetic force acting amounts to Hev , and if X is the strength of the electrostatic field the electrostatic force exerted upon the electron is Xe , so that when these two forces just balance we have—

$$Hev = Xe$$

$$\text{or} \quad v = \frac{X}{H}$$

By means of this equation one can determine the velocity of

the cathode rays. In a highly exhausted tube this may attain to a velocity approximately one-third of the velocity of light, that is to say, about 60,000 miles per second. This is many thousand times the velocity of a hydrogen molecule at ordinary temperature, or indeed at any temperature yet realised.

Now let us suppose that the magnetic field is removed. The corpuscles are acted upon by the electrostatic field, which causes their path to be deflected. The behaviour is analogous to that of a bullet travelling horizontally at a high speed, and at the same time falling towards the earth owing to gravitation. We know that in the time t the bullet will fall by the amount $\frac{1}{2}gt^2$, where g is the acceleration of gravity. In the case of the corpuscle, since the downward force (supposing it to act downwards) is Xe , and since in general, force = mass \times acceleration, or acceleration = $\frac{\text{force}}{\text{mass}}$, it follows that if m is the mass of a corpuscle, the downward acceleration is $\frac{Xe}{m}$, and the distance through which it falls in time t is $\frac{1}{2}\frac{Xet^2}{m}$. If l is the horizontal distance travelled with velocity v during the time t , then $t = \frac{l}{v}$. Hence the vertical distance over which the particle falls (which is measured by observing the vertical displacement of the phosphorescent spot on the glass) is given by the expression

$$\frac{1}{2} \cdot \frac{Xe}{m} \cdot \frac{l^2}{v^2}$$

Now we can measure d , the vertical displacement of the phosphorescent spot, and as we already know v , X , and l , it is possible to calculate the ratio $\frac{e}{m}$ from the equation—

$$\frac{e}{m} = \frac{2d}{X} \cdot \frac{v^2}{l^2}$$

In this manner it has been found that the ratio $\frac{e}{m}$ is the same

for all cathode rays provided they are not moving with a velocity approaching the velocity of light. Further, this ratio is independent of the chemical nature of the electrodes, and likewise of the nature of the gas which still remains in the tube. The value for $\frac{e}{m}$ on the c.g.s. system electromagnetic units is 1.7×10^7 . Previous to the examination of the cathode rays, the largest value known for the ratio of the charge to the mass was that met with in the case of the hydrogen ion in aqueous solution. We have already seen from Perrin's work that the charge on such an ion is 4.19×10^{-10} electrostatic units, and the mass of one hydrogen atom (or ion) is 1.47×10^{-24} gram, so that the ratio of charge to mass is 3×10^{14} . To convert this into c.g.s. electromagnetic units it is necessary to divide by the factor 3×10^{10} , so that the ratio of $\frac{e}{m}$ for the hydrogen ion is 1×10^4 . Hence, for the corpuscle of the cathode rays the same ratio is 1700 times greater. This must arise in one of two ways; first, either the charge on the corpuscle is 1700 times greater than the charge on the hydrogen ion, the mass of the ion and the corpuscle being assumed identical, or, secondly, the charges may be identical but the mass of the corpuscle only $\frac{1}{1700}$ of that of the hydrogen ion. To settle which of these alternatives is the correct one it is necessary to determine the charge e on a single corpuscle.¹

MAGNITUDE OF THE CHARGE ON AN ELECTRON OR CORPUSCLE.

To determine this quantity use is made of the discovery of C. T. R. Wilson that if electrically charged particles are

¹ For a fuller discussion of the method of obtaining the ratio $\frac{e}{m}$ for the corpuscle the reader is referred to Sir J. J. Thomson's *Electricity and Matter*, or *The Corpuscular Theory of Matter*. An "Elementary treatment of the motion of a charged particle in a combined electric and magnetic field," is given by W. B. Morton, *Proc. Physical Soc.*, 21, 300, 1908.

introduced into a vessel containing supersaturated vapour—say water vapour—condensation of the vapour will occur upon the charged particles, which act as nuclei for the droplets of the cloud which falls slowly under the action of gravity. The experiment is easily carried out if a source of X rays or if some radium salt be brought near the vessel, since the rays shot off by the radium salt penetrate the walls of the vessel and ionise the gas inside, thereby producing a number of positively and negatively electrified particles which act as nuclei. The negative particles are simply atoms which have gained an electron, the positives being the charged atomic “residues” left after the removal of an electron from the neutral atom. C. T. R. Wilson has shown that condensation takes place more easily upon the negative particles than upon the positive ones, and it is possible, as was shown by H. A. Wilson, to so adjust the degree of supersaturation that condensation takes place *only* upon the negative ones. The rate v at which the cloud falls is given, according to Stokes, by the expression—

$$v = \frac{2}{9} \cdot \frac{gr^2\rho}{\eta}$$

where g is the acceleration of gravity, η the viscosity of the gas, ρ the density of the droplet, and r the radius of one of the droplets. It is thus possible to determine r , and therefore the volume of each droplet. We can also determine the total volume of water condensed when we know the extent of supersaturation, which in turn can be obtained if we know the dimensions of the vessel and the travel of the piston fitted into the vessel—the piston being employed to bring about the state of supersaturation in the vessel which contains air and unsaturated water vapour. It is therefore possible to calculate the total number of droplets in the cloud. Now it is easy to measure the total charge on the cloud by measuring the ionisation current which occurs when a certain potential difference is applied to the ionised gas. We can thus obtain the charge on each droplet, and assuming that each droplet is condensed on a nucleus having a single charge e , we have at once the charge carried by an electron.

An alternative mode of procedure was adopted by H. A. Wilson, who observed the rate of fall of the cloud under gravity alone and then under the simultaneous action of gravity and a known electrostatic field. If v_1 denotes the velocity of fall under gravity alone, and v_2 the velocity under gravity plus an electric force Xe , where X is the strength of the field or the potential gradient, then we have the relation—

$$\frac{v_1}{v_2} = \frac{mg}{mg + Xe}$$

Introducing Stokes' expression for v_1 , namely—

$$v_1 = \frac{2}{9} \cdot \frac{gr^2\rho}{\eta}$$

where ρ is the density of a droplet and $m = \frac{4}{3}\pi r^3\rho$, we obtain, on combining the above equations, the expression—

$$e = \left\{ \frac{4}{3}\pi \left(\frac{9\eta}{2g} \right)^{\frac{3}{2}} \right\} \frac{X}{\rho^{\frac{1}{2}}} \frac{(v_2 - v_1)v_1^{\frac{1}{2}}}{\rho^{\frac{1}{2}}} \quad \dots \quad (11)$$

By the aid of the above and other modifications, it was found that $e = 3.1 \times 10^{-10}$ electrostatic units, or 1×10^{-20} electromagnetic c.g.s. units. Now we have seen that the charge on a hydrogen ion is 4.19×10^{-10} electrostatic units, so that within the limits of experimental error (which in the earlier determinations such as the one given were fairly wide), we are justified in concluding that *the charge e upon a corpuscle is identical with that on a monovalent electrolytic ion*. But the ratio of $\frac{e}{m}$ for the corpuscle is 1700 times that for the ion; we must therefore conclude that the mass of the ion or atom is 1700 times greater than that of the corpuscle. Since the mass of one hydrogen atom is 1.47×10^{-24} gram, it follows that the mass of an electron or corpuscle is 8.7×10^{-28} gram.

The above value for e is, however, not a very accurate one. It has been redetermined recently by Millikan with great care. The results are briefly as follows.

MILLIKAN'S DETERMINATION OF " e " BY A MODIFICATION OF THE WILSON CLOUD METHOD. (See Millikan, *Phil. Mag.*, [6] 19, 209, 1910.)

Millikan attempted to obtain a sufficiently strong electric field to exactly *balance* the force of gravity upon the cloud of charged droplets. It was found that this could only be partially realised, but instead Millikan succeeded in holding *individual charged drops* suspended by the field from 30 to 60 seconds. The droplets which it was possible to thus suspend always contained multiple charges ($2e$ to $6e$). The procedure is simply to form a cloud as previously described, the source of the ionisation employed by Millikan being a radium salt. The electric field is then excited. The drops which have charges of the same sign as that of the upper plate or too weak charges of the opposite sign, rapidly fall, while those which are charged with too many multiples of sign opposite to that of the upper plate are jerked up against gravity to this plate. The result is that after a lapse of six or eight seconds the field of view in the observation telescope has become quite clear save for a relatively small number of drops which have just the right ratio of charge to mass to be held suspended by the electric field. The observations were made by means of a telescope having three equally spaced horizontal hairs in the eyepiece, the distance between the extreme hairs being about one-third of the distance between the two charged plates producing the electric field. The cross hairs were set near to the lower plate (the electric field being on), and as soon as a stationary droplet was found somewhere above the upper cross hair, it was watched for a few seconds to make sure it was not moving, *i.e.* falling or rising, and then the electric field was thrown off. The drop was then timed in its fall under gravity as it passed across the three hairs. This method affords a check on any evaporation of the drop, if such occurs, since in this event the rate of travel between the first and second hair would be faster than that between the

second and third.¹ In general the times taken were the same. We can apply equation (11), remembering that in the balanced state, $v_2 = 0$ and X is negative in sign (since it opposes gravity). We thus obtain the relation—

$$e = 3.422 \times 10^{-9} \frac{X}{g} (v_1)^3$$

Millikan carried out a large series of determinations of e by this method, the extreme values being 4.87×10^{-10} and 4.56×10^{-10} . The mean value adopted is $e = 4.65 \times 10^{-10}$ *electrostatic units*. For the purpose of comparison, attention may be drawn to the following alternative values of e obtained by different methods:—

1. Planck calculated $e = 4.69 \times 10^{-10}$, using Kurlbaum's radiant energy data (see Part III. (Vol. II.)).

2. Rutherford and Geiger (*Proc. Roy. Soc., A*, 81, 141, 161, 1908) obtained 4.65×10^{-10} by counting the number of α particles emitted by a known quantity of radium salt and measuring the total electrical charge carried by these particles.

3. Regener's value 4.79×10^{-10} (*Sitzungsbericht d. k. preuss. Akad.*, 38, 948, 1909), obtained by counting the number of scintillations produced by a known amount of polonium and measuring the total charge carried.

4. Begeman obtained $e = 4.67 \times 10^{-10}$ as a mean of a large number of measurements carried out by the Wilson method.

Millikan does not consider Perrin's value of N (which, as already pointed out, leads to a value for e) as sufficiently accurate.² The most probable value for e obtained up to the year 1910 is, according to Millikan, 4.69×10^{-10} electrostatic units. Using this number, he has calculated N to be 61.8×10^{22} and the number of molecules per cubic centimetre of a gas at normal temperature and pressure to be 2.76×10^{19} . The mass of one hydrogen atom is also easily calculable and comes out to be 1.62×10^{-24} gram.

¹ Remember that we are supposed to be considering the motion of a droplet which is moving at a *steady* rate, the *acceleration* due to gravity being balanced by the frictional resistance of the medium.

² Perrin has, however, replied to Millikan's criticism. See *Phil. Mag.*, 19, 438, 1910.

MILLIKAN'S "OIL DROP" METHOD OF DETERMINING THE CHARGE ON AN ELECTRON. (Millikan, *Physical Review*, **32**, 349, 1911. For a summary of the method and the results obtained, see Millikan, *Trans. Amer. Electrochem. Soc.*, **21**, 185, 1912.)

The following brief account is given partly in Millikan's own words.

An apparatus was set up consisting of two metal plates, separated by an air layer across which a known potential difference of several thousand volts could be thrown. The upper plate was pierced about its centre with a small pinhole, thereby communicating to a large air chamber above into which a very fine spray of oil droplets could be pumped. The air between the plates was ionised by means of X rays, thereby giving rise to an equal number of positive and negative gaseous "ions." An oil drop on passing through the pinhole entered the region of ionised air, and ultimately caught one or more of the ions. Even before entering this region the oil drop was electrically charged (by friction in the spraying process), and hence it could be made to move up or down in the field of view, according as the electrical field was thrown on or off. On catching an ion the rate at which the drop was moving upward in the electrical field was observed to change abruptly, and by measuring the velocity of the same drop over an extended series of time intervals, the number of charges communicated to it could be obtained. The precision of the measurements and the certainty with which the unitary or discrete nature of electricity follows as a result of the measurements can best be appreciated by inserting the results of a single experiment. Column I. gives the successive times in seconds taken by the droplet in falling under the action of gravity alone between two fixed cross hairs in the eyepiece of the telescope, the actual distance of fall being 0.5222 cm. It will be seen that these numbers are exceedingly concordant. Column II. gives the successive times which the same droplet required to rise the same distance under the influence of the electrical field, when a potential of 5051 volts was applied.

Column I.	Column II.
13·6	12·5
13·8	12·4
13·4	21·8
13·4	34·8
13·6	84·5
13·6	85·5
13·7	34·6
13·5	34·8
13·5	16·0
13·8	34·8
13·7	34·6
13·8	21·9
13·6	
13·5	
13·4	
13·8	
13·4	
<hr/>	
Mean 13·595	

It will be seen that after the second trip up (in the electric field) the time changed from 12·4 to 21·8, indicating (since the droplet was *positively* charged by the spraying process) that a *negative* ion had been caught from the air. (If the particle had been completely discharged it would, of course, not have moved upward at all but downward, with a velocity indicated by the figures of column I.) The next recorded time in column II. is 34·8, which indicates that another negative ion has been caught. The next time period, 84·5, indicates the capture of still another negative ion. This charge was held for two trips, when the time interval changed back again to 34·6, showing that a positive ion had now been caught—(Millikan considers the loss of an electron by the droplet as unlikely)—this positive charge being precisely the same in magnitude as that of the negative ion which before caused the inverse change in the time interval, *i.e.* from 34·8 to 84·5. To find the absolute value of these charges, it is necessary to know the mass m of the droplet. Their *relative* magnitudes can be obtained, however, in the first instance, without determining m . Thus, let us consider the up and down movement separately. The downward force due to

gravity is mg , the upward force due to the electrical field is Xe . Hence if v_1 is the velocity downward due to gravity, and v_2 the velocity upward due to the excess of the electrical field over the gravitational, we find—

$$\frac{v_1}{v_2} = \frac{mg}{Xe - mg} \quad \text{or} \quad e = \frac{mg}{Xv_1}(v_1 + v_2) \quad (12)$$

Thus the charge added to the droplet at an encounter is proportional to the *change* produced in the sum of the two velocities by the capture, for m , g , v_1 and X are constant. Now, the change in this sum produced by the capture of the ion which caused the time interval in column II. to change from 34·8 to 84·5 was 0·00891 cm. per second,¹ and the successive values of this quantity arranged in order of magnitude were 0·04456, 0·05347, 0·06232, 0·07106, 0·08038. If now electricity is “atomic” in structure (*i.e.* consists of small units), all the different charges appearing in this experiment should be exact multiples of the elementary unit of charge, which means that all the numbers given above should be exact multiples of something. Dividing the last five numbers by 5, 6, 7, 8, and 9 respectively, one obtains the series: 0·008912, 0·008911, 0·008903, 0·008883, and 0·008931, which are all seen to be within one-fifth of 1 per cent. of the value 0·00891, which is the change in the sum of the speeds produced by the capture of the first ion. Hence the charge added to the droplet on capturing this ion is itself the elementary unit; the total charge at any moment borne by the droplet during the course of the experiment being an even multiple of this

¹ In the first case (time = 34·8 secs. against gravity), since the actual distance travelled is 0·5222 cm.—

$$v_1 + v_2 = \left(\frac{0\cdot5222}{13\cdot595} + \frac{0\cdot5222}{34\cdot8} \right).$$

In the second case—

$$v_1 + v_2 = \left(\frac{0\cdot5222}{13\cdot595} + \frac{0\cdot5222}{84\cdot5} \right)$$

and hence the difference is—

$$0\cdot5222 \left(\frac{1}{34\cdot8} - \frac{1}{84\cdot5} \right) = 0\cdot00891 \text{ cm. per second.}$$

number. Nearly one thousand different drops have been examined in the manner indicated, some of them being oil (a non-conductor), some being glycerine (a semi-conductor), and some mercury (a good conductor), and in all cases the initial charge placed upon the drop by the frictional (spraying) process, and all of the dozen or more charges which resulted from the capture by the drop of a larger or smaller number of ions have been found to be exact multiples of the smallest charge caught from the air. This is the most conclusive proof of the "atomic" structure of electricity.

By means of equation (12) Millikan obtained very accurate values for $\frac{e}{m_d}$, where m_d is the mass of the droplet in this case.

To obtain e it is therefore necessary to determine the mass m_d . Stokes' expression for the velocity of fall under gravity, namely,

$v_1 = \frac{2}{9} \cdot \frac{gr^2}{\eta}$, allows of our calculating the radius, and therefore

the volume and mass of the droplet—assuming the density of the droplet to be that of the oil in bulk. As a result of special experiments, however, Millikan found that the above expression was not quite accurate for this case. He therefore modified it slightly by the addition of an empirical term, and with this more accurate form calculated r , and eventually m_d . The value of e was thus directly obtained. As a mean of a very large number of values, Millikan gives the value (*British Ass. Rep.*, 1912)—

$$e = 4.4775 \times 10^{-10} \text{ electrostatic units,}$$

the error not exceeding 1 part in 1000.

An interesting fact discovered by Millikan in experiments somewhat similar to those described, in which the droplet was held in suspension, was that only *one* electron is detached from a given gas molecule when the gas is ionised. The oil droplet was "in a veritable shower of the positive residues of the molecules split up by the rays," yet in no case did a capture of one of these residues communicate more than one electrical unitary charge. If two electrons had been ionised off a molecule, the positive residue would carry two unitary

charges, and would communicate these to the droplet on collision. Since out of 500 "catches," 496 were certainly single unitary charges, the remaining four being doubtful, the conclusion is that the process of ionisation consists in the expulsion of one electron from a molecule.

THE "OIL DROP" METHOD OF STUDYING BROWNIAN MOVEMENT IN GASEOUS MEDIA.

Perrin's observations on Brownian movement refer to particles suspended in a *liquid* medium. Millikan (*l.c.*) has succeeded by his electrified oil drop method in determining the extent of the movement of the drop when balanced in air by having the electric field adjusted to the gravitational field. The arrangement is similar to that already described, the only modification being that of enclosing the apparatus in order to permit of lowering the air pressure, since the Brownian movement of the droplet only becomes measurable at low pressures. Several hundred determinations were made of the distance travelled by the droplet in a vertical direction in ten seconds, for as we have already seen Einstein's theory is developed in such a way that only movements along one axis have to be considered. The expression for the mean-square-displacement Δ^2 is—

$$\Delta^2 = \frac{2RT\tau}{NC}$$

where C is the frictional resistance of the medium. Millikan's final expression, based on a more rigid treatment¹ than that given earlier, takes the form—

$$\Delta = \sqrt{\frac{4}{\pi} \cdot \frac{RT\tau}{NC}} \cdot \cdot \cdot \cdot \cdot \quad (13)$$

The essential advantage of Millikan's method lies in the elimination of C . This is done by observing the successive displacements of the *balanced* drop and then to destroy the balance and measure the rate of fall of the drop (under

¹ See H. Fletcher, *Le Radium*, 8, 279, 1911.

gravity alone) and under gravity *assisted* by the electrical field. Suppose that the drop moves down under gravity (force = mg) with a velocity v_1 . We have then the relation $mg = Cv_1$. Substituting this value of mg in equation (12), we obtain—

$$e = \frac{C}{X}(v_1 + v_2)$$

and combining this with equation (13) we can eliminate C , obtaining finally the relation—

$$\Delta = \sqrt{\frac{4}{\pi} \cdot \frac{RT(v_1 + v_2)\tau}{XNe}}$$

With the help of this equation Millikan calculated the value of \sqrt{Ne} , which came out 1.698×10^7 electrostatic units, this being the total quantity of current carried by one gram-mole of a univalent substance. Now \sqrt{Ne} is known very accurately in the case of silver from measurements of the quantity of current required to precipitate one gram equivalent of silver from solution. The value is 1.702×10^7 electrostatic units. This agreement to less than one-fourth of 1 per cent. between the values of \sqrt{Ne} may be taken as proving that the value of e on the gas ions is the same as the charge on the univalent ion in solution, provided the kinetic theory of Brownian movement is assumed to be correct; or *vice versa*, if the identity of the charge on the gaseous ion and the electrolytic ion is considered as established by the work of Townsend and others, then Millikan's experiments establish in a very rigid manner the correctness of the kinetic treatment of Brownian motion.

THE RÔLE OF ELECTRONS IN METALS.

Metals are noted for the property which they possess of conducting electricity and heat. Since the introduction of the concept of the electron considerable advance has been made in our knowledge of the solid state from this standpoint. Unfortunately there is no space in a book of this nature to consider this problem further. Mention can only be made of one very

important relation which the electron theory as applied to metals (after certain simplifications have been introduced) predicts, namely, that the ratio of the thermal conductivity to the electrical conductivity should be a *constant* independent of the nature of the metal, and depending directly upon the absolute temperature. This relation, which was known as a purely empirical one under the title of the Wiedemann-Franz Law, possesses very considerable experimental support. For the method of deducing the relation referred to the reader must consult Sir J. J. Thomson's books already mentioned, and especially the papers of O. W. Richardson, to whom we are indebted for the greatest advances in this field. (O. W. Richardson, "Electron Theory of Metallic Conduction," *Transactions of the Amer. Electrochem. Soc.*, 21, 69, 1912, gives a good summary of the present position.) It should be pointed out that rather remarkably the development of the unitary theory of radiant energy (see Part III. (Vol. II.)) in the hands of Nernst and Lindemann has led these authors to the conclusion that electrons are *not* the main cause of thermal conduction. The evidence is therefore at the present time somewhat conflicting.

THE VARIOUS SOURCES OF CORPUSCLES OR ELECTRONS.

Cathode rays are not the only source of electrons. Mention has already been made that electrons are given out (along with other sorts of radiation) by radium and other radioactive materials during their decomposition. They are also given out, though to a much less extent, by other metals, such as the alkalies and alkaline earths, as well as by some amalgams, especially when these substances are heated or exposed to light—light, in fact, causes the expulsion of electrons from most metals, particularly if the light is of very short wave length (ultra-violet), such effects being known as "photo-electric effects." Electrons are also emitted when salts are vaporised in gas flames. The important thing is that whatever its source the ratio of $\frac{e}{m}$ for an electron is constant.

It seems natural, therefore, as Sir J. J. Thomson says, "to regard it as one of the bricks of which atoms are built up."

Regarding the *origin* of the mass of an electron little can be said here beyond the fact that Sir J. J. Thomson has shown that its energy, and therefore its mass, is really due to energy of the ether—the medium which fills all space and transmits light and electro-magnetic waves in general. But the whole question of what we mean by the "ether" has been rendered decidedly vague by the new work on radiation (*cf.* Part III. (Vol. II.)).

THE STRUCTURE OF THE ATOM.

Since an atom is electrically neutral, it is evident that it must contain a quantity of positive electricity equivalent to the sum of the charges on the electrons. We know very little indeed about the positive electricity, and the simplest assumption to make, therefore, is that it occurs as a sphere of uniform density throughout which the electrons are distributed.¹ This sphere attracts the corpuscles to its centre, their mutual repulsions tending to drive them away from one another, so that the "fabric" of the atom as a whole is in equilibrium when the repulsions just balance the attraction. The problem first studied by Sir J. J. Thomson is to find how electrons will distribute themselves in a sphere of positive electricity when successive additions are made to the number of electrons in the system. The problem soon becomes too difficult to treat mathematically if we consider the distribution in *three* dimensions in space. A simpler case is to consider the distribution in *one* plane (two dimensions) only—the plane being one which passes through the centre of the atom. The results obtained by Sir J. J. Thomson, though not complete, are sufficient to indicate in a general way the solution of the problem. If the system contains one electron it will evidently go to the centre of the sphere. If two electrons are present they will take up

¹ Recent work of Rutherford and others (*Phil. Mag.*, 1913, 1914) points to the existence of a positive nucleus round which electrons rotate in various orbits.

positions at two points A and B, situated along a straight line which passes through the centre O of the sphere, so that $OA = OB =$ one-half the radius of the sphere. Three electrons will distribute themselves at the apices of an equilateral triangle, any side of which is equal to the radius of the sphere. Four electrons cannot be in equilibrium in one plane. If we consider for a moment the distribution in tridimensional space the equilibrium arrangement is reached when the electrons are at the corners of a regular tetrahedron, whose centre is the centre of the sphere, and whose side is equal to the radius of the sphere. Returning to the case of distribution in one plane, we find that five electrons will be in equilibrium in single ring formation, *i.e.* at the corners of a regular pentagon. Six electrons will, however, not be in equilibrium at the corners of a regular hexagon. Instead, one electron goes to the centre and the remaining five form a regular pentagon. This is a "two-ring" system. Similarly eleven electrons distribute themselves, so that there are two forming the inner "ring" and nine in the outer. With successive additions one finds that the two-ring system becomes unstable, and a three-ring system makes its appearance. This happens when seventeen electrons are present, and the three-ring system persists until we reach thirty-two electrons, when a four-ring system appears. In this way we can go on adding electrons, thereby building up "atoms" of higher atomic weight. The above results (and others in which still greater numbers of electrons are considered) were obtained by mathematical analysis. They can also be demonstrated by a very ingenious experimental analogy due originally to Mayer. For this purpose a number of small magnetised needles take the place of the corpuscles. The needles, which are all magnetised in the same way, are stuck through corks and floated upon water. The rôle of the sphere of positive electricity is taken by a large magnet suspended above the water, with its N pole pointing downwards if the S poles of the magnetised needles point upwards. On adding the needles one at a time various equilibrium configurations are obtained very similar to those already given. From one to five magnets, the single ring is stable; with six magnets

one goes to the centre, the remaining five being equally distributed around it, and so on.

An important feature of the distribution of electrons is the recurrence of similar *types* at intervals. Thus the "atom" containing one electron has this electron at the centre. The "atom" containing six electrons has again one at the centre, the remainder forming the outer ring of the two-ring system, 1,—5. The "atom" with seventeen electrons is three-ring, one electron being in the centre, then a ring of five, and lastly a ring of eleven; thus, 1,—5,—11. The "atom" of thirty-two electrons is four-ring, one electron in the centre, then a ring of five, then a ring of eleven, and lastly a ring of fifteen, that is, 1,—5,—11,—15. Similarly, the "atom" which has forty-nine electrons in five rings is built up on the following type: 1,—5,—11,—15,—17. The "atoms" which consist of 1, 6, 17, 32, and 49 electrons have therefore a similar constitution. We would expect that physical and chemical properties which must depend ultimately upon atomic structure would likewise be similar in these cases. At the same time the "atoms" in which the number of electrons lies between six and seventeen, or between seventeen and thirty-two, or between thirty-two and forty-nine, are not built up on the 1,—5,—11,—15,—17 plan. The properties of these intermediate members would, therefore, differ from those previously considered. We thus see that the electron theory leads one to expect that there will be a *periodicity* in the properties of the atoms as the atomic weight increases. This is simply the Mendeleef-Meyer Periodic Law. It is clear that we have here strong evidence in favour of the electronic structure of atoms, since this theory predicts at least qualitatively the law which forms the most fundamental generalisation of systematic chemistry.¹

As regards the *actual* number of electrons in atoms information is scanty. Attempts which have been made in this direction indicate, however, that the number is small roughly of the order of the relative atomic weight, *i.e.* the sodium atom

¹ As regards valency, which appears to be the lines of force produced by the transfer of an electron, the reader is referred to N. Friend's *Valency* in Sir W. Ramsay's series.

contains twenty-three electrons. It is clear, therefore, since an electron possesses only $\frac{1}{1700}$ part of the mass of a hydrogen atom, that the main source of the mass of an atom must be due to the *positive* electricity contained in it. This brings us to the consideration of some very ingenious speculations regarding the *rôle* played by the positive electricity in the building up of atoms.

NICHOLSON'S THEORY OF THE STRUCTURE OF ATOMS.
(*Phil. Mag.*, 22, 864, 1911.)

The main difference between this theory and that of Sir J. J. Thomson lies in the question of the distribution of the positive charge. We have already seen that Sir J. J. Thomson considers the atom as consisting of a number of electrons dispersed throughout a sphere of positive electricity; this assumption being indeed made for the purpose of simplicity of treatment rather than as actually representing the physical facts. Nicholson's view is that the positive electricity exists in the atom like the electrons in *discrete portions*, each of uniform density; and further, these units are *small* in radius compared even with the electrons themselves. At the same time, these "positives" are regarded as the source of nearly the whole mass of the atom. The atomic system is, therefore, planetary. "In a complex atom, built up of simpler systems, the assemblage of positive charges is in many respects similar to the assemblage of electrons which revolve round them, and it is not unlikely that many of the positive charges would also revolve. But they are not all of the same size, although the difference in size is not great. Their mass is so great that a disturbance which could expel one of them from an atom would also expel many of the attendant electrons, and it would be impossible to isolate a positive charge." This is in agreement with experiment up to the present (1914) as regards the isolation of the positive unit, although evidence of the existence of such is afforded indirectly.¹ Evidence in

¹ See R. W. Wood, *Phil. Mag.*, February, 1908.

favour of Nicholson's theory is afforded by Sir William Ramsay's discovery that Radium Emanation or Niton—itsself the newest member of the series of monatomic gases—gives rise to the element Helium. "Unless the constituents of this atom already exist as a group in unstable equilibrium with other groups, in the atom of the emanation, it is difficult to imagine by what means it can be detached as such when a really definite conception of the process is intended." Evidently the difficulty is extreme on Sir J. J. Thomson's view of the atom, nor is it less on Rutherford's view that the atom is a simple Saturnian system involving only a single positive nucleus.

In building up the atoms of the elements Nicholson finds it necessary to postulate the existence of three protyles, namely, hydrogen, a hypothetical element which he calls "nebulium,"¹ and another hypothetical element which he calls "protofluorine." The hydrogen atom is assumed to possess three electrons, nebulium four, and protofluorine five. The element containing two electrons he identifies with coronium, an element in the sun's corona, but does not appear to require this in building up the other (known) elements.

As regards atomic weights, according to Nicholson we must accept the fact that all inertia (*i.e.* all mass) is due to electric charges in motion, which we have already mentioned as having been shown to be the case by Sir J. J. Thomson in connection with the mass of an electron.

The weight of an atom always determined from its inertia may be regarded as the sum of the inertias of all its positive and negative charges. If the positive charges have a much smaller radius their inertia will greatly outweigh that of the electrons, and we may neglect the latter for the present. The motions to which a positive nucleus is subject will always be slow compared with the velocity of light. Let r be the radius of the positive, and let e be the charge upon an electron. If there are n electrons in a neutral atom of a primary simple substance (containing only one nucleus) the positive charge is ne , and the inertia of the nucleus and, therefore, of the whole

¹ Nebulium is perhaps *not* hypothetical, see page 66.

atom approximately is proportional to $\frac{n^2 e^2}{r}$ by the usual formula ¹ for slow motions. If the positive electricity has uniform volume density, its volume is proportional to ne , therefore its radius r is proportional to $(ne)^{\frac{1}{3}}$, or $n^{\frac{1}{3}}$, since e is a constant. *Thus the inertia or mass of the atom is proportional to $n^{\frac{5}{3}}$ from the above formula.* The mass of a compound atom containing several nuclei associated with rings of electrons will be proportional to $\Sigma n^{\frac{5}{3}}$. Assuming that the hydrogen atom has three electrons, the relative weights of the atoms of the primary substances are—

Coronium	$n = 2, n^{\frac{5}{3}} = 3.1748$
Hydrogen	$n = 3, n^{\frac{5}{3}} = 6.2403$
Nebulium	$n = 4, n^{\frac{5}{3}} = 10.079$
Protofluorine	$n = 5, n^{\frac{5}{3}} = 14.620$

Taking the atomic weight of hydrogen to be 1.008, the above substances have the following relative atomic weights :—

¹ An uncharged body of mechanical mass m , travelling with velocity v , possesses kinetic energy $\frac{1}{2}mv^2$. If the body is electrically charged, it sets up a magnetic field round it in virtue of its motion, and this field contains energy given by the expression $\frac{1}{3} \cdot \frac{e^2 v^2}{r}$, where e is the charge and r the radius of the body. The energy which has to be supplied to keep the charged sphere in motion is $\frac{1}{2}mv^2 + \frac{1}{3} \cdot \frac{e^2 v^2}{r}$, or $\frac{1}{2} \left(m + \frac{2}{3} \cdot \frac{e^2}{r} \right) v^2$. The body acts, therefore, as if it possessed the mass $\left(m + \frac{2}{3} \cdot \frac{e^2}{r} \right)$. A rough analogy is afforded by the motion of a particle through a viscous fluid, for, as the particle moves, it carries some of the fluid along with it, thereby apparently increasing its own mass. If r were one or two centimetres, the term $\frac{2}{3} \cdot \frac{e^2}{r}$ would be quite negligible compared to the mechanical mass m . If r is of the order of the diameter of an electron, Sir J. J. Thomson has shown that m is negligible compared to $\frac{2}{3} \cdot \frac{e^2}{r}$. Hence the same conclusion is justifiable in connection with the small positive nuclei of Nicholson. For this reason the mass or inertia is placed proportional to the term $\frac{n^2 e^2}{r}$.

Coronium	0.51282	
Hydrogen	1.008	(Oxygen = 16)
Nebulium	1.6281	
Protofluorine	2.3615	

We can now consider compound atoms built up out of these primaries. Nicholson, as already mentioned, did not find coronium necessary apparently for this purpose; a fact which is somewhat surprising. Neglecting the mass of the electrons in comparison with the mass due to the positive nuclei (although n in the expression $n^{\frac{5}{2}}$ is actually the number of electrons), Nicholson suggests that the helium atom is made up of one atom of nebulium (Nu), and one atom of protofluorine (Pf). Writing this in the form of a chemical equation—



Atomic weight of Nu = 1.6281

Atomic weight of Pf = 2.3615

Sum = 3.9896, At. weight of He = 3.99

According to Nicholson, "there is a fairly general suspicion that many of the elements may be composed of helium and hydrogen." Thus boron (atomic weight 11) might be $2\text{He} + 3\text{H}$. When the helium "group" (on the above hypothesis) enters into the composition of another more complex atom it is not implied that this group actually exists as in free helium atoms, but its two component groups Nu and Pf may be present, though occupying different relative positions from those which they occupy in the helium atom. A few typical instances of Nicholson's method of building up compound atoms may be given.

Argon.—The atomic weight is 39.88. $10\text{He} = 39.9$.

Carbon.—The atomic weight is 12.00. The combination ($2\text{He} + 4\text{H}$) gives the atomic weight 12.008.

Oxygen.—The atomic weight is 16.00. The combination ($3\text{He} + 4\text{H}$) gives 15.996.

Fluorine.—The atomic weight is 19.0. The combination ($3\text{He} + 7\text{H}$) gives 19.020.

Neon.—The atomic weight is 20.21. The combination ($6\text{Pf} + 6\text{H}$) gives 20.21.

“Apparently the group $(3\text{Pf} + 3\text{H})$ or $(\text{PfH})_3$ has considerable significance in atomic structure, according to the present theory.”

For further applications of this theory the reader must consult the original paper. It must, of course, be pointed out that at the present stage these considerations are of a speculative nature. In the opinion of the writer they represent, however, the best of the numerous attempts already made to elucidate the constitution of atoms of elements. Nicholson's speculations are of particular interest in view of the recent experiments of Collie and Patterson, to which reference will be made shortly. The real importance of Nicholson's views lies in the fact that a definite *rôle* is assigned to the positive charge resident in the atom, and, at the same time, the number of electrons (n) enters in a logical manner into the term for the atomic weight, although this “weight” is essentially due to the positive nuclei. It should be noted that the most crucial test of the above views is to be found in the calculation of the atomic weights of elements which possess small atomic weights, such as helium, lithium, beryllium, etc.; in the case of elements with higher atomic weight, which might possibly be built up out of more than one combination of the protyles, the assigned structure is of less importance.

H. W. Nicholson (*Proc. Roy. Astron. Soc.*, **72**, 49, 1911) has calculated the chief spectral lines of the hypothetical element nebulium, which, according to his theory, contains four electrons rotating round a positive nucleus whose charge is $4e$. This arrangement represents a neutral atom. If one electron is missing, the other three can take up equidistant positions and rotate in a new orbit, the system consisting now of one atom of nebulium with single positive charge in excess (the nucleus being still $4e$). Also the atom may acquire a negative charge by taking up one or more electrons. The neutral, positive, and negative atoms respectively give rise to different lines in the spectrum. Nicholson found that the spectrum lines of certain nebulae—principally the Orion nebula—which have hitherto been assigned to an unknown element or elements could, with the exception of two lines, be accounted for quantitatively by the vibrations of the atomic system charged and uncharged, which he has called nebulium. This result affords a certain amount of evidence in favour of Nicholson's theory of the structure of atoms.

THE DISINTEGRATION OF THE ATOM. RADIOACTIVITY.

We are already familiar with the existence of small electrically charged particles as being the principal constituents of all atoms. Further, we have seen that negatively charged particles—the electrons—may be obtained from a variety of sources. A source of special interest is the group of chemical substances known as the radioactive elements. The typical radioactive metals are: uranium, actinium, radium, and thorium. Radioactive substances, as the name implies, are characterised by the property of emitting radiations which can be detected by the electrical or photographic effects produced by them. These radiations have been divided into three classes— α rays, β rays, and γ rays.¹

The α rays are positively charged particles shot off from the radioactive substance with considerable velocity. They can, with difficulty, be deviated by a strong magnetic field, and the direction of deviation indicates the sign of their charge. Their mass is comparable with that of the helium atom (four times that of the hydrogen atom, and each carries two positive charges ($2e$)). In their passage through a gas they cause ionisation of the gas,² which thereby becomes a conductor of electricity. This ionising power depends upon the velocity of the particles, a good ionising agent such as the α particles not possessing extremely great velocity, and therefore not possessing a very great penetrating power. Thus, by enclosing the radioactive substance in a glass tube, the α radiations are completely stopped with sufficiently thick walls.

Besides α particles, some radioactive substances emit negatively charged particles called β rays, which are identical with cathode rays or electrons. The velocity with which they are emitted varies greatly from case to case. These rays are deviated easily by a magnetic field, and in the opposite sense to that experienced by the α rays. Their mass is only $\frac{1}{1700}$

¹ A further variety, known as Δ rays, has also been investigated.

² For an account of the mechanism of the ionisation process the reader should consult Townsend's book on *Ionization of Gases by Collision*.

part of one hydrogen atom. They possess much greater penetrating power than α rays, and therefore in their passage through a gas produce much *less* ionisation. These β rays escape, at least in large proportion, through the glass walls of the tube enclosing the radioactive substance.

In addition to the *material* radiations (α and β rays) some radioactive substances can also give rise to a third kind of radiation called γ rays, which are characterised by the property of being non-deviable by a magnetic field. At the present time there are conflicting views regarding the actual "constitution" of these rays. At any rate, they are not a stream of material particles as the α and β rays are. One view is that they consist of ether pulsations analogous to Röntgen rays, assuming the latter to *be* pulsations. γ rays are the most penetrating type of radiation, and are therefore least effective in producing ionisation in a gas.

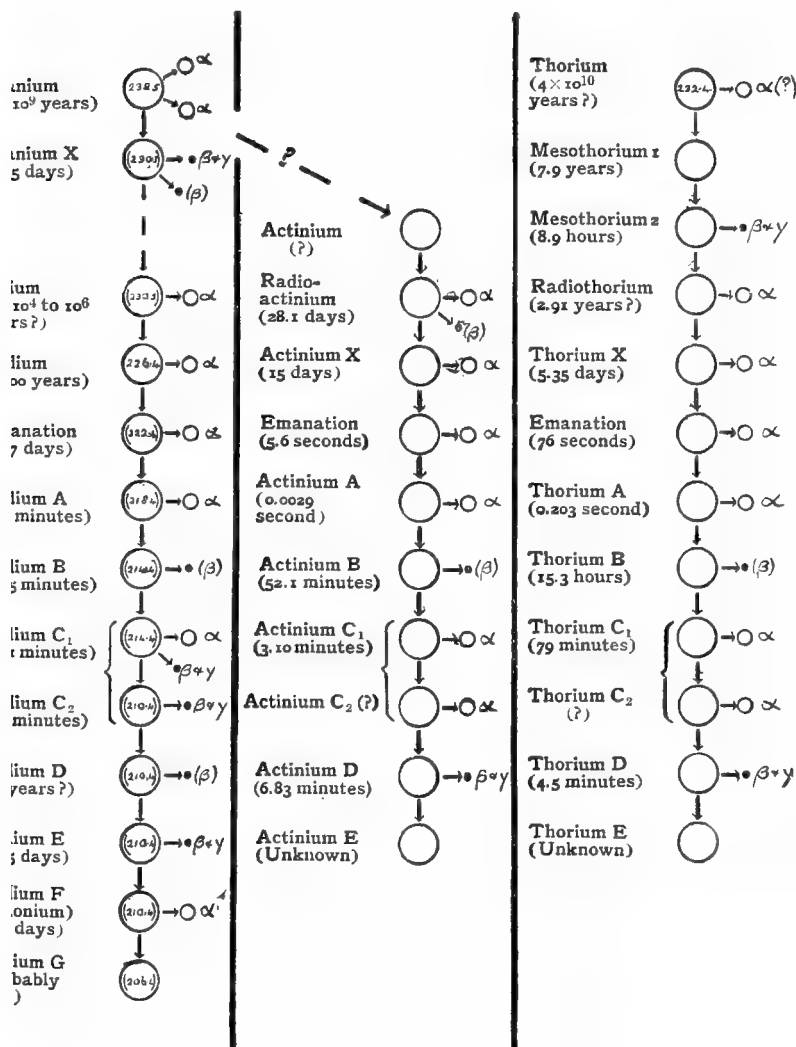
A large number of successive radioactive transformations have been observed up to the present time. At each transformation one practically always finds one or other of the above types of rays given out, the γ ray generally accompanying the expulsion of a β particle. In the accompanying table is given the chronology of these transformations as far as they are known at present. Each substance is identified not by "chemical" properties, the quantity present being exceedingly small, but by the duration of its radioactivity. A single isolated radioactive body will gradually lose its activity, the law of radioactive decay being the simple exponential one—

$$I = I_0 e^{-\lambda t}$$

where I_0 is the initial activity of the body, I the activity at a time t , and λ a constant which characterises the substance in question. The activity is measured by the rate at which a gold-leaf electroscope is discharged. From the observed rate of decay one can calculate λ , and from this one can easily find the time required for a given radioactive body to lose one-half of its radioactivity. This time is called the "half-life" period.

The table is taken by permission from F. Soddy's monograph on *The Chemistry of the Radio Elements*, in Findlay's

series. The time periods given in connection with each substance represent the "periods of average life," which are 1.45 times the half-life period. The nature of the rays emitted by each product is also indicated.



There are a number of gaps in the above table, indicating that there are other products which have as yet remained undiscovered. Further, it is now recognised that side-chain products have to be anticipated; that is, the production of two or more substances apparently simultaneously from one parent substance. The theory which was first advanced by Rutherford to account for the existence of radioactivity and the relations of radioactive substances to one another, is that the radioactive atom disintegrates or breaks down, emitting a ray of some kind, and leaving a residue of smaller atomic weight which possesses properties differing from the parent substance. This residue in its turn may disintegrate in a similar manner. It is evident that the expulsion of an α particle causes a much greater decrease in the atomic weight of the residue than the expulsion of a β ray, since the mass of an α particle is approximately six thousand times as great as that of an electron. An adequate account of radioactivity in general cannot be given within the compass of a few pages. A few typical examples of the rate of radioactive change will be taken up later as illustrations of chemical kinetics; but for further details the reader must consult Rutherford's book on Radioactivity, or Soddy's *Interpretation of Radium* and *The Chemistry of the Radio Elements*, or Makower's *Radioactive Substances*.

As regards the significance of the phenomenon of radioactivity from the standpoint of the structure of the atoms of the elements the most interesting fact is the observation made by Ramsay and Soddy in 1903, that radium emanation (which is a gas, and has been shown recently by Ramsay and Gray to belong to the rare gas group under the name niton) obtained from radium bromide gradually developed the *helium spectrum*, giving the characteristic yellow line. This is the first instance of the transmutation of the elements, and it shows that the electrical grouping constituting the helium atom must have been present originally in the heavier radium atom. It is now known with considerable certainty that the helium atom is simply an α particle which has lost its (double) positive charge. Helium can therefore be formed at all

those stages at which α particles are emitted. Such evidence as this is, of course, strongly in favour of an electrical corpuscular constitution of all atoms, and this is borne out by the fact that radioactivity is not confined to a few metals, but is—although to a much smaller degree—a general property of ordinary metals as well. In the same connection, and especially with regard to Nicholson's theory of the structure of the atom, the recent discovery of Collie and Patterson (*Journ. Chem. Soc.*, 103, 419, 1913) of "the presence of neon in hydrogen after the passage of an electric discharge through the latter at low pressures" is of the utmost importance. In this work all conceivable precautions were taken to avoid any leakage of air into the apparatus. One of the final forms of the apparatus consisted of a double-walled glass tube, the discharge being passed through the *inner* tube which contained hydrogen, the outer tube being at a high vacuum. After continuous sparking for some hours it was discovered that quite appreciable quantities of helium and neon were present in the *outer* tube, and likewise a smaller amount of neon in the *inner*. During the progress of the sparking the greater bulk of the hydrogen itself had disappeared. Although the authors are careful to avoid the expression of any views regarding the mechanism of the production of these gases, the experimental fact remains as an extremely suggestive one from the standpoint of atomic structure and transmutability of so-called "elementary" atoms.

CHAPTER II

Distribution of molecules in space—Physical equilibrium—The continuity of the liquid and gaseous states, from the kinetic standpoint.

HAVING considered the actual existence of molecules, it is necessary to go a little more closely into the question of how these distribute themselves in space under given conditions of temperature and pressure. Although the subject will be treated in the present instance from the standpoint of purely "physical" equilibrium, it must not be forgotten that "chemical" effects, such as polymerisation of molecules on the one hand, or dissociation on the other, enter in certain cases: and indeed when we find that the system under consideration exhibits divergencies in behaviour from what might be expected upon purely physical or mechanical grounds, we are practically forced to conclude that the discrepancies are due to more strictly "chemical" change. It is, however, of extreme importance to treat the problem—at least as far as we are able—from the standpoint of molecular mechanics, as has been done, to a large extent in the so-called "theory of the continuity of state." Gases, liquids, and vapours will be considered—solids are omitted here owing to the meagre information we possess in regard to them.¹

The word "state" refers to a somewhat arbitrary division of matter in relation to a particular kind of molecular aggregation and orientation under given conditions of temperature and pressure, such molecular arrangements and relations being characterised by the presence or absence of certain physical

¹ In Part III. (Vol. II.) will be found an account of recent work done on the constitution of solids in relation to the new theory of *energy quanta*.

properties. Each "state" represents the *equilibrium* distribution of the molecules forming the system. The fact that at one and the same temperature two such different types of equilibrium distribution as that represented by a liquid and its saturated vapour exist is sufficient to indicate that the attractive and repulsive forces operating between molecules are by no means simple, and indeed very little is known about it. We recognise three states of matter—solid, liquid, and gaseous. With the general characteristics of these states the reader is assumed to be familiar.

THE BEHAVIOUR OF GASEOUS SYSTEMS.

We have already seen in the introductory chapter that the law of Boyle (1662) and the law of Charles or Gay Lussac (1808) may be combined in the equation—

$$\frac{pv}{T} = \text{constant}$$

The numerical value of the constant depends obviously upon the units employed and the mass of gas considered. The molecular weight of a gas in grams we shall call the gram-molecule. The gram-molecule is the same multiple of the actual weight of a molecule, or the gram-molecule contains the same number of actual molecules for all substances whose molecules are normal, that is molecules neither polymerised nor dissociated. If we take the gram-molecule as our unit of mass and restrict our consideration to *gases* whose molecules are normal, we know by the hypothesis of Avogadro that the gram-molecule of any gas at a given temperature and pressure must occupy one and the same volume. Taking the gram-molecule as the unit of mass, it is usual to denote the constant in the above expression by R ; that is

$$\frac{pv}{T} = R \text{ or } pv = RT$$

It has been found that 1 gram-molecule of a gas at

273° absolute, and at 1 atmosphere pressure occupies a volume of 22.38 liters. Hence the value of

$$R = \frac{pv}{T} = \frac{22.38 \times 1}{273} \frac{\text{liter atmosphere}}{\text{degree}}$$

or since 1 atmosphere = 10^6 dynes per square cm. approx., it follows that

$$\begin{aligned} 1 \text{ liter atmosphere} &= 1000 \times 10^6 \frac{\text{dynes} \times \text{c.c.'s}}{\text{cm.}^2} \\ &= 10^9 \text{ ergs.} \end{aligned}$$

Further 1 calorie = 4.2 joules = 4.2×10^7 ergs,

so that employing the calorie instead of the liter atmosphere as the unit of energy, we obtain for R the value of 1.98 approx.

The expression $pv = RT$ is known as "the gas law," and is taken as the criterion—or rather part of the criteria¹—of a *perfect gas*. All actual gases approximate more or less closely to this ideal state, but none obey the gas law absolutely. We shall consider the behaviour of a few actual gases in some detail.

If Boyle's Law held rigidly for actual gases, then at constant temperature the product pv ought to be constant whatsoever the value of p . That pv is not quite independent of p , even for gases such as hydrogen, nitrogen, oxygen, etc., is evident from the following data obtained by Amagat (*Annales de Chim. et de Phys.*, [6] 29, 68, 1893). For gaseous substances such as ethylene and carbon dioxide, which at ordinary temperatures are much nearer their "critical point" than the gases above mentioned, the value of pv varies very much with change in p .

¹ The remaining criterion of a perfect gas is that Joule's Law shall be obeyed, *i.e.* that the total energy shall be independent of the volume (*cf.* Part II. (Vol. II.), Chap. III.).

Values of pv for hydrogen and nitrogen.—[Note: The product pv is arbitrarily taken as unity under one atmosphere and at 0° C.]

Hydrogen.			Nitrogen.		
p in atmospheres.	$t = 0^\circ$ C (pv).	$t = 99.25^\circ$ (pv).	p in atmospheres.	$t = 0^\circ$ C (pv).	$t = 199.5^\circ$ C (pv).
1	1.0000	—	1	1.0000	—
100	1.0690	—	100	0.9910	—
150	1.1030	1.4770	150	1.0085	1.8620
200	1.1380	1.5135	200	1.0390	1.9065
400	1.2830	1.6590	400	1.2570	2.1325
600	1.4315	1.8040	600	1.5260	2.3840
800	1.5775	1.9490	800	1.7980	2.6400
1000	1.7200	2.0930	1000	2.0685	—

The following data refer to ethylene and carbon dioxide. The unit value is arbitrarily assigned to the product pv when p is 1 atmosphere and the temperature is 0° C. The values at this temperature are not reproduced owing to the fact that this being below the "critical temperature" liquefaction takes place at the higher pressures, the system becoming heterogeneous (liquid + vapour) thereby giving a discontinuous curve.

Ethylene (gaseous).			Carbon dioxide (gaseous).		
p in atmospheres.	10° C. (pv)	100° C. (pv)	p in atmospheres.	50° C. (pv)	100° C. (pv)
1	—	—	1	—	—
50	0.4200	1.1920	50	0.9200	1.2065
100	0.3305	1.0050	100	0.4910	1.0300
150	0.4590	0.9240	125	0.3950	0.9470
200	0.5850	0.9460	150	0.4190	0.8780
300	0.8270	1.1330	200	0.5000	0.8145
400	1.0585	1.3560	400	0.8515	1.0385
1000	2.3205	2.6425	600	1.1865	1.3655
			1000	1.8140	1.9990

If ethylene obeyed the gas law $pv = RT$ rigidly, the value of pv on the above scale at 10° C. would have been 1.0366, at

100° , 1.3663. Similarly, the p_v for carbon dioxide would have been 1.1832 and 1.3663 at 50° and 100° respectively. The behaviour of the four substances, hydrogen, nitrogen, ethylene, and carbon dioxide with respect to Boyle's Law is shown

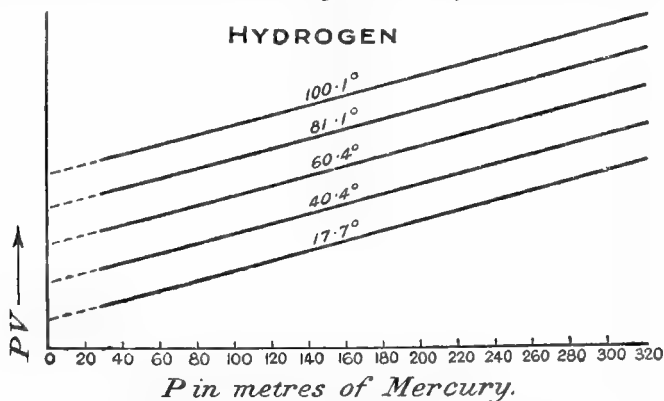


FIG. 10.

(E. H. Amagat, *Ann. Chim. et de Physique*, [5] 22, 370, 1881.)

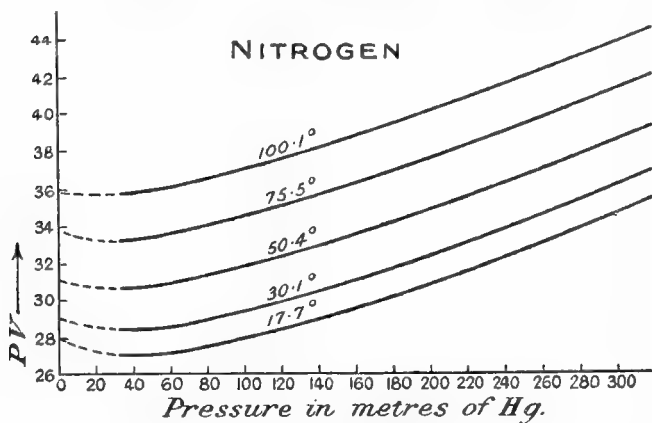


FIG. 11.

(E. H. Amagat, *ibid.*)

graphically on the accompanying diagrams (Figs. 10, 11, 12 and 13).

It will be observed that in no case is a horizontal line obtained such as Boyle's Law requires. Hydrogen alone

throughout the temperature range given shows a steady rise in the value of pv as p increases; the other gases show first a decrease in pv to a minimum value followed by a rise for still higher values of p . The divergences from Boyle's Law are due to two causes, (1) the volume of the molecules themselves, though

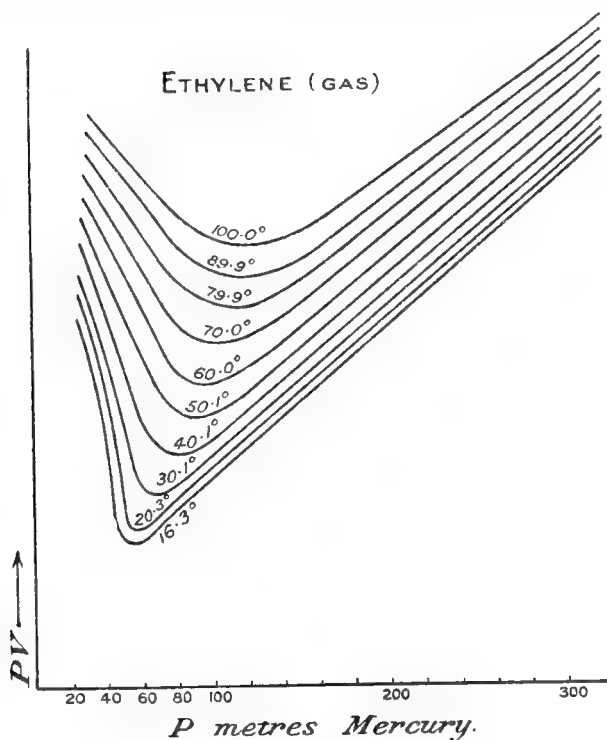


FIG. 12.

(E. H. Amagat, *ibid.*)

small compared to the total space occupied by the gas, is not zero, and in many cases is by no means negligible; (2) there are forces of attraction sometimes of considerable magnitude operating between the molecules. These two effects in general oppose one another, and which will predominate depends on the conditions (T and p) of the system. The

two effects referred to are taken account of, as we shall see, by terms involving two constants a and b in van der Waals' equation of state. The increase in $p v$ with increasing p simply means that the gas is not compressible enough, *i.e.* v does not decrease as much as it would if the gas were perfect. The molecules themselves can only be regarded as very slightly compressible compared with the actual system, gas or liquid, in

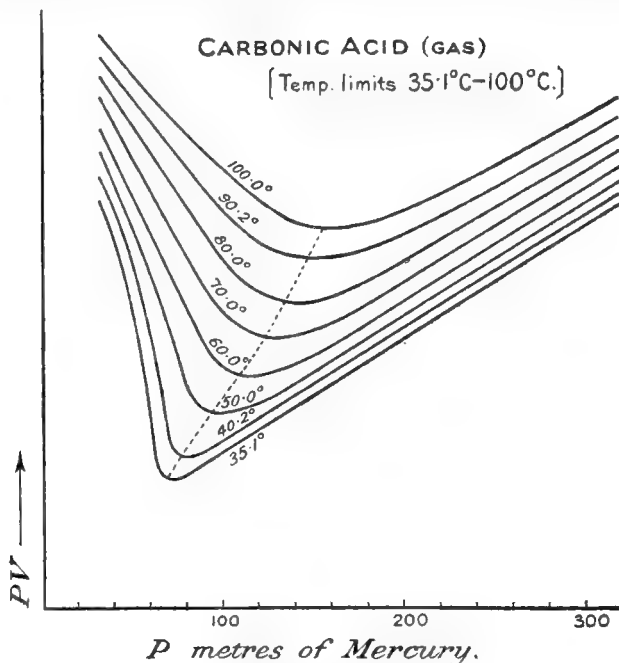


FIG. 13.

(E. H. Amagat, *Ann. Chim. et de Physique*, [5] 22, 370, 1881.)

which the molecules are present. In fact, if we were able to compress a portion of matter sufficiently until the molecules came into contact with one another, any further increase of pressure would only have an infinitesimal effect upon the volume, and the product $p v$ would *rapidly* increase with increase in p . The other effect mentioned, namely, the attraction between the molecules, has the opposite effect, that

of making the gas too compressible (compared with the perfect gas) by drawing the molecules together. Owing to this attraction, the value of $p v$ should diminish with increase in p . This is seen to be the initial resultant effect in ordinary gases (with the exception of hydrogen) up to certain pressure values, when the molecular-volume correction term predominates and the $p v$ values begin to rise. This type of curve, in which a minimum is exhibited, may also be realised in the case of hydrogen, provided we work at a temperature considerably lower than that for which the data were quoted. This is considered in a more quantitative manner later.

BEHAVIOUR OF SYSTEMS CONSISTING OF GAS AND LIQUID.

So far we have only considered systems which are entirely gaseous. It is well known, however, that under certain conditions a highly compressed gas may become partially liquid, condensation going on *without* increase of pressure but with great decrease of volume until the system becomes homogeneous once more, being now entirely liquid. The principle known as the *continuity of state* was first enunciated by Andrews to apply to such phenomena. According to Andrews, there is no essential difference between states of matter, the liquid and gaseous states being simply widely separated stages in a continuous series of changes. Andrews was the first to investigate the conditions under which a gas could or could not be liquefied. In this way he introduced the concept of *the critical state* involving *critical temperature*, *critical pressure*, and *critical volume*. Andrews found experimentally in the case of gases such as carbon dioxide, nitrous oxide, ammonia, and ether vapour, that there existed a certain temperature—the critical temperature—above which it was impossible to liquefy the gas, no matter how great the pressure. The minimum pressure which was just sufficient to cause the gas to liquefy at the critical temperature was called the critical pressure, and the volume of unit mass of the gas at the critical temperature and pressure was called the critical volume.

The following table (taken partly from S. Young's *Stoichiometry*,¹ partly from P. Walden, *Zeitsch. physik. Chem.*, vol. 66, 1909, and partly from G. Rudorff, *Annalen der Physik*, [4] vol. 29, 1909) gives the values of the critical temperature in degrees centigrade, the critical pressure in atmospheres, and the critical density, that is the reciprocal of the critical volume, for a few substances:—

Substance.	Critical temperature, ° C. t_c	Critical pressure, p_c (atmos.).	Critical density $= \frac{1}{v_c}$
Helium	— 268	2·26	0·066
Neon {	lower than } — 218	—	—
Argon	— 117·4 (— 122·44)	50·6	0·509
Krypton	— 62·5	54·2	0·775
Xenon ²	+ 16·6	58·2	1·155
Hydrogen	— 238	13·4 to 15	0·043
Nitrogen	— 146	35	0·299
Oxygen	— 119	50·8	0·4 to 0·65
Ethylene	+ 10·1	51·0	0·22 to 0·36
Carbon dioxide .	31·35	72·9	0·464
Ammonia	130	115·6	0·239
Ether	193·8	35·6	0·2625
Carbon tetrachloride	283·15	44·97	0·5576
Isopentane . . .	187·8	32·92	0·2343
Benzene	288·5	47·89	0·3045
Ethyl acetate . .	250·1	38·0	0·3077
Ethyl alcohol . .	243·1	63·0	0·2755
Water	360	195·5	0·2078
Hydrochloric acid .	52	86 to 96	0·61 to 0·462

A brief account of the methods whereby p_c , v_c , and t_c may be obtained will be given later.

It will be evident from the foregoing discussion that the simple gas law does not hold for actual gases or vapours. In the case of liquids the law breaks down entirely. In view of the close connection between the liquid and gaseous states

¹ Young has recently published the recalculated data upon the vapour pressures, specific volumes, heats of vaporisation and critical constants of thirty pure substances (mainly organic) (*Proc. Roy. Dub. Soc.*, 12 [N.S.], 374-443, 1910).

² Patterson, Cripps and Whytlaw-Gray, *Proc. Roy. Soc.*, 86 A, 579, 1912.

other expressions have been proposed as possessing a more general applicability, these being called "characteristic equations," or "equations of state." Before considering some of these, however, it is convenient to consider still further some of the experimental data upon pressure, volume, and temperature in the case of carbon dioxide and isopentane, both liquid and gaseous.

AMAGAT'S DATA (*l.c.*) ON THE VARIATION OF pv WITH p FOR CARBON DIOXIDE AT TEMPERATURES BELOW THE CRITICAL POINT.

p in atmospheres.	pv at 0° C.	pv at 30° C.
1	1.0000 (arbitrary unit)	—
50	0.1050	0.7750
100	0.2020	0.2550
200	0.3850	0.4400
400	0.7280	0.7950
600	1.0495	1.1275
1000	1.6560	1.7480

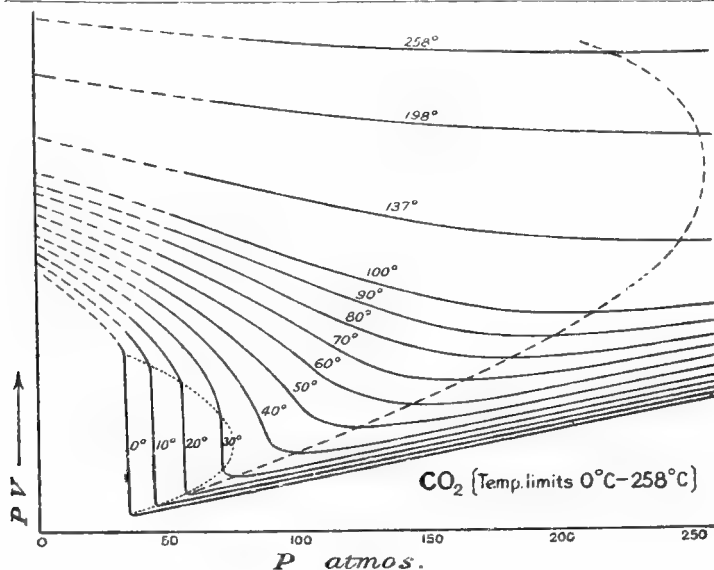


FIG. 14.

At low pressures the system is entirely gaseous, at higher
T.P.C.—I. G

pressures it becomes liquid. The product pv is not even approximately constant. The accompanying diagram (Fig. 14) illustrates the relation of pv to p over the temperature range 0° – 258° C.

If CO_2 were a perfect gas the diagram would consist of a series of horizontal lines.

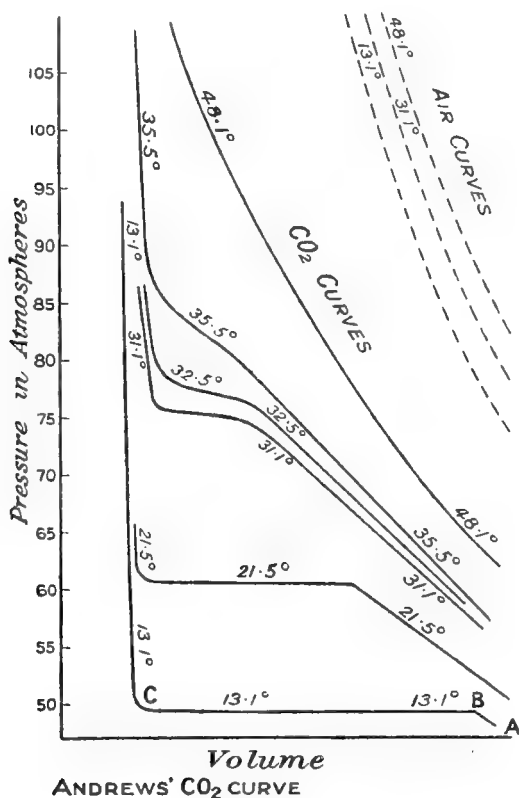


FIG. 15.

Let us now look at the behaviour of the same substance from a slightly different standpoint, namely, the variation of v itself with p at a series of different temperatures. This was first done by Andrews, and his curves are reproduced in Fig. 15. Each line represents the relation between p and v at a given

temperature, such lines being known as the isothermals of the system. The same *mass* of carbon dioxide is employed throughout. Consider the isothermal corresponding to the temperature 13.1°C . At low pressures the volume (A) is large. As the pressure is increased the volume decreases nearly proportionally, *i.e.* Boyle's Law is very nearly obeyed. When a certain volume (B) is reached partial liquefaction takes place and the pressure of the system remains constant while the volume diminishes, the isothermal being horizontal. This state of things holds good until the system has so decreased in volume that it becomes entirely liquid at (C). To cause any further decrease in v a large increase of pressure is required, so that the isothermal becomes nearly vertical. At the temperatures 21.5°C . and 31.1°C . the same kind of behaviour is observed except that at the higher temperatures the horizontal portion of the isothermal (that part which corresponds to the simultaneous existence of liquid and vapour) becomes rapidly shorter, and, in fact, at 32.5° there is no horizontal portion at all, *i.e.* the system does not liquefy. The critical temperature of CO_2 lies between 31.1° and 32.5° . At higher temperatures, therefore, the system is homogeneous and gaseous, no matter what pressure may be employed to compress the gas. The higher the temperature the more nearly do the isothermals approximate (compare the isothermal at 48.1°) to those which would be given by a perfect gas (rectangular hyperbolæ). For the sake of comparison, Andrews includes the curves for air. At ordinary temperatures air approximates fairly closely to the behaviour of a perfect gas, since the critical temperatures of nitrogen and oxygen lie very much below room temperature.

To return to the case in which liquid and gas (*i.e.* saturated vapour) are in contact, the gradual change in the density of each phase with temperature and the approximation of the phases to identity which is realised at the critical point are apparent from the following results obtained by Amagat (*l.c.* 1893) in the case of carbon dioxide :—

t° centigrade.	Density of liquid.	Density of saturated vapour.	Pressure exerted by system.
0	0.914	0.096	34.3 atmos.
5	0.888	0.114	39.0 "
10	0.856	0.133	44.2 "
15	0.814	0.158	50.0 "
20	0.766	0.190	56.3 "
25	0.703	0.240	63.3 "
28	0.653	0.282	67.7 "
29	0.630	0.303	69.2 "
30	0.598	0.334	70.7 "
30.5	0.574	0.356	71.5 "
31	0.536	0.392	72.3 "
31.25	0.497	0.422	72.8 "
31.35	0.464	0.464	72.9 "

Hence critical temperature = 31.35° C. ; critical pressure = 72.9 atmospheres ; critical volume = $\frac{1}{0.464}$ c.c.

If the values of the densities of liquid and vapour are plotted against temperature, one obtains a closed curve of the shape shown in Fig. 16.

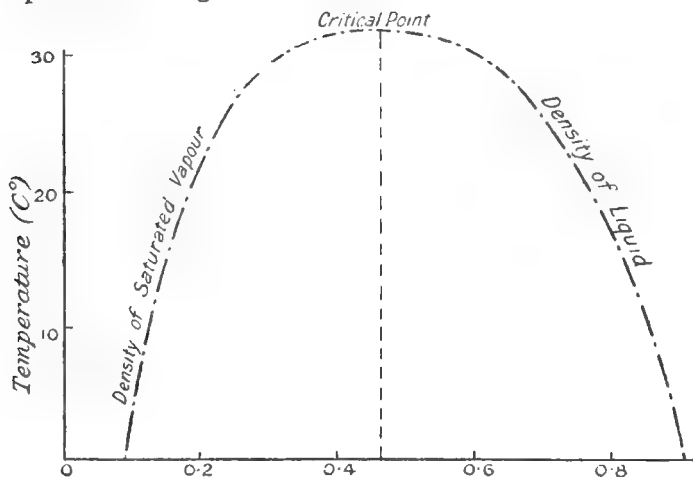


FIG. 16.

If the *mean* value of the density of liquid and density of vapour at each temperature be likewise plotted, it will be found

that the points lie on a straight line (Fig. 16, dotted line), so that if S_m denotes the mean density at a temperature t , it may be written in the form—

$$S_m = S_0 + \alpha t$$

This linear relation is known as the law of Cailletet and Mathias, or the law of the rectilinear diameter. It holds fairly accurately for a number of substances, though it must not be regarded as being strictly true in general. Thus for the case of isopentane, which has been most thoroughly examined from the standpoint of the continuity of state by S. Young (compare Young's *Stoichiometry*), it has been found that a more accurate relation is—

$$S_m = S_0 + \alpha t + \beta t^2$$

Determination of the Critical Constants t_c , p_c , v_c .—The critical temperature and pressure may be obtained as follows :

A bent tube containing some of the liquid over mercury is placed in a heating bath and the temperature gradually raised (Fig. 17). In the case of carbon dioxide, Andrews (*Phil. Trans.*, Part II., p. 575, 1869; *ibid.*, Part II., p. 421, 1876) gives the following description of what takes place when the system consisting of liquid CO_2 in contact with saturated CO_2 vapour in a sealed tube, is gradually warmed to the region of 31°C . : "... the surface of demarcation of the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout the entire mass." Andrews called the temperature at which these phenomena appear the "critical point." The critical temperature is therefore that at which the surface of demar-



FIG. 17.

(From Young's *Stoichiometry*.)

cation disappears, and this may be obtained directly from the temperature of the bath. Similarly from the difference in level of the mercury in the two limbs, the critical pressure may

be read off directly. The critical volume might be read off directly from the observed volume, but the possibility of error is great because of the great compressibility of a substance at its critical point, whereby any slight alteration of pressure has an enormous effect upon the volume. Young, therefore recommends, as the most trustworthy means of obtaining the critical volume, the application of the law of Cailletet and Mathias, or rather the more accurate relation—

$$S_m = S_0 + \alpha t + \beta t^2,$$

which gives for the critical density S_c the expression—

$$S = S_0 + \alpha(t_c - t_0) + \beta(t_c - t_0)^2$$

in which S_c is simply $\frac{1}{v_c}$.

For further details of the experimental difficulties met with in the determination of critical values the reader is referred to Young's *Stoichiometry*.

Young (*Zeitsch. physik. Chem.*, 29, 223, 1899) has collected a large amount of data in the case of isopentane, partly with the object of seeing how far the Cailletet-Mathias rule ($S_m = S_0 + \alpha t$) holds good in this case. A few of his values are reproduced below.

ISOPENTANE.

Temperature centigrade.	Density of liquid.	Density of vapour (saturated).	Mean density observed.	Mean density calculated.
10	0.6295	0.0016	0.3156	0.3152
50	0.5881	0.0060	0.2970	0.2970
100	0.5278	0.0203	0.2741	0.2743
150	0.4445	0.0583	0.2514	0.2516
170	0.3914	0.0932	0.2423	0.2425
180	0.3498	0.1258	0.2378	0.2380
183	0.3311	0.1422	0.2366	0.2366
185	0.3142	0.1575	0.2358	0.2357
186	0.3028	0.1677	0.2353	0.2352
187	0.2857	0.1834	0.2346	0.2348
187.4	0.2761	0.1951	0.2356	0.2346
critical temp. } 187.8	—	—	—	0.234

$$\text{Critical volume of 1 gram} = \frac{1}{0.234} = 4.266 \text{ c.c.}$$

JAMES THOMSON'S EXTENSION OF ANDREWS' THEORY OF THE CONTINUITY OF STATE (*Proc. Roy. Soc.*, 20, 1, 1871).

The following is a brief account of Thomson's theory as far as possible in his own words. Andrews showed that the ordinary gaseous and liquid states are only widely separated states of the same condition of matter, and may be made to pass the one into the other by a course of continuous physical changes representing nowhere any interruption or breach of continuity. The saturated vapour pressure curve or "boiling point" curve comes to an end at the critical point. "Now, it will be my [Thomson's] chief object in the present paper to state and support a view which has occurred to me, according to which it appears probable that, although there be a practical breach of continuity in crossing the line of boiling points from liquid to gas or from gas to liquid, there may exist in the nature of things, a theoretical continuity across this breach having some real and true significance. This theoretical continuity from the ordinary liquid state to the ordinary gaseous state must be supposed to be such as to have its various courses passing through conditions of temperature pressure and volume in unstable equilibrium for any fluid matter theoretically conceived as homogeneously distributed while passing through the intermediate conditions.

"It is first to be observed that the ordinary liquid state does not necessarily cease abruptly at the line of boiling points, as it is well known that liquids may, with due precautions, be heated considerably beyond the boiling temperature for the pressure to which they are exposed." Referring to Andrews' isothermals for CO_2 —the p and v being the ordinates—Thomson points out that the system may still remain liquid under conditions in which it should consist partly of liquid and partly of vapour. Thus in the diagram (Fig. 18), the curve GA, which shows the volumes of the *liquid* under various pressures, does not necessarily change abruptly into AC when the point A is reached, but may extend *continuously* for some distance as is shown by the dotted line AB. Analogous

extended so that a curve such as CDEFBA represents the hypothetical relations between p and v in place of the horizontal line AC. The part of the curve DEFB has never been realised experimentally. In spite of this, Thomson's view has the great advantage that since it substitutes a *continuous* curve in place of a discontinuous one, it renders possible the application of an *equation* which will reproduce the values of p and v for the liquid as well as for the gaseous state. (It is, of course, impossible to get an analytical expression which will correspond to discontinuous curves such as *actually* represent the relations between p and v below the critical point.) Thomson discusses these hypothetical isothermals as follows: "Let us suppose an indefinite number of curves each for one constant temperature to be drawn. . . . Now we can see, that as we pass from one curve to another in approaching toward the critical point *from* the *higher* temperatures, the tangent to the curve at the steepest point or point of inflexion is rotating [compare the curves for CO_2 , Fig. 15, at the temperatures 48.1° , 35.5° and 32.5° respectively] so that its inclination to the plane of the co-ordinate axes for pressure and temperature increases until at the critical point it becomes a right angle. Then it appears very natural to suppose that in proceeding onwards past the critical point to curves successively for lower and lower temperatures, the tangent at the point of inflection will continue its rotation, and the angle of its inclination, which before was acute, would now become obtuse. It seems much more natural to make such a supposition as this than to suppose that in passing the critical point from higher into lower temperatures, the curved line should break itself asunder and should come to have a part of its conceivable continuous course absolutely deficient. It thus seems natural to suppose that in some sense there is continuity in each of the successive curves, such as those drawn in the accompanying diagram as dotted curves uniting continuously the curves for the ordinary gaseous state with those for the ordinary liquid state."

Thomson says further: "The overhanging part of the curve from E to F seems to represent a state in which there would be some kind of unstable equilibrium; and so, although

the curve there appears to have some important theoretical significance, yet the states represented by its various points would be unattainable throughout any ordinary mass of the fluid. It seems to represent conditions of coexistent temperature, pressure, and volume, in which, if all parts of a mass of fluid were placed, it would be in equilibrium, but out of which it would be led to rush partly into the rarer state of gas and partly into the denser state of liquid by the slightest inequality of temperature or of density in any part relatively to other parts."

ANALYTICAL EXPRESSIONS ("EQUATIONS OF STATE") PROPOSED TO REPRODUCE THE BEHAVIOUR OF GAS AND LIQUID SYSTEMS.

I. THE EQUATION OF RAMSAY AND YOUNG.

This expression applies only to the case in which the *volume of the system is kept constant*. The expression which gives a relation between the temperature and pressure under this condition may be written thus—

$$p = kT - c$$

where p is the pressure exerted by the system,¹ k and c are constants to be determined by experiment, and T the absolute temperature. The relation may be expressed more generally thus—

$$p = Tf(v) - F(v)$$

where f and F are different functions of the volume. If v is kept constant, $f(v)$ and $F(v)$ are necessarily constants.

It will be seen that this equation is really a substitute for the Gay-Lussac expression (which states that $p = kT$ when v is constant in the case of a perfect gas), the modification being the introduction of the term c . It is not, however (in the first form given), at the same time a substitute for Boyle's law, so that the Ramsay and Young equation is necessarily limited in application, the constants k and c , for example, being only constant (by definition) as long as the system is kept at constant volume. For different volumes different numerical values must be assigned to k and c . Amagat (*Compt. Rend.*, 94, 847, 1882)

¹ The system considered must necessarily be homogeneous, either entirely liquid or entirely gaseous. This is true for all the "equations of state."

found that the relation held accurately for CO_2 and C_2H_4 for the gaseous state, but only approximately so for the liquid state. Ramsay and Young, on the other hand (*Phil. Mag.* [5] 23, 435, 1887), found that the expression held good for ethyl ether for the liquid as well as for the gaseous state. Barnes came to the same conclusion, and Ramsay and Young showed further

ISOCORES FOR ETHER.

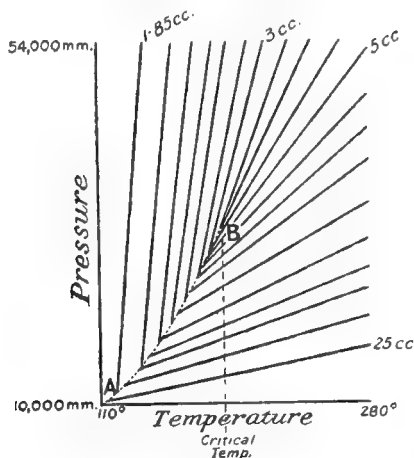


FIG. 19.

The Ramsay-Young Law. Isochores are practically straight lines. The dotted line AB represents saturated vapour pressures at various temperatures. To the left of this the system is liquid (small values of v); to the right the system is gaseous. The critical temperature marks the superior limit of the saturated vapour-liquid curve. The isochores are equally straight in liquid and vapour states, *i.e.* the Ramsay-Young law applies to both states.

that the relation holds approximately for methyl, ethyl, and propyl alcohols, but that considerable discrepancies are observed in the case of water (see Ramsay and Young, *Phil. Mag.*, August, 1887; *Phil. Trans.*, A. 137, 1889; *Phil. Trans.*, A. 107, 1892). To show the applicability of the equation, we may take some of the data given by Ramsay and Young (*Phil. Mag.* [5] 23, 435, 1887) in the case of ethyl ether. If the expression holds true, the pressure ought to be a linear function of the absolute temperature, the volume being kept constant. The diagram (Fig. 19) shows a number of the

isochores thus obtained. An isochore is a curve on a pt diagram, the pressure and temperature being variable, the volume invariable. It will be observed that the curves are very nearly straight lines.

Another method of investigating the equation is to calculate the constants for any given volume. If we differentiate the expression with regard to T , we obtain—

$$\left(\frac{dp}{dT}\right)_v = k$$

The value of $\frac{\partial p}{\partial T}$ is simply the tangent to the pt curve at any given temperature, and may thus be read graphically provided the data refer to constant volume. By substituting the value of k in the expression $p = kT - c$ for any two values of T and p (the volume being the same for both), one can solve for c . Having thus obtained k and c (corresponding to a given volume), values of p at other temperatures, but keeping the volume the same, may be calculated and compared with those observed. Other volumes may now be selected, and the corresponding k and c values obtained. By procedure such as this it is possible to see what are the limits of applicability of the law. The following table contains some of the data obtained by Ramsay and Young (*l.c.*) in the case of ether:—

ETHER AT 197° C., *i.e.* A FEW DEGREES ABOVE THE CRITICAL POINT.

Volume of 1 gram.	Pressure in mm. of mercury.	Pressure calculated by the R. and Y. equation.
33° 17	10108	10055
38° 07	8972	8965
47° 84	7312	7320
57° 59	6166	6130
67° 33	5356	5340
77° 05	4718	4735
86° 75	4219	4220
96° 44	3820	3820

A more thorough investigation of the equation was undertaken by S. Young (*Zeitsch. physik. Chem.*, 29, 223, 1899) in the

case of isopentane. The following values of $k = \left(\frac{dp}{dT}\right)_v$ are taken from the very extended tables given by Young.

(a) Volume of the system = 4.0 c.c., this being kept constant throughout the temperature range.

Temperature, centigrade.	$k = \left(\frac{dp}{dT}\right)_v$	Temperature, centigrade.	$k = \left(\frac{dp}{dT}\right)_v$
187.8 (critical)	405	210	443
190	418	220	439
195	428	230	462
200	434	240	446
205	430		

(b) Volume of system = 50 c.c.

Temperature, centigrade.	$k = \left(\frac{dp}{dT}\right)_v$	Temperature, centigrade.	$k = \left(\frac{dp}{dT}\right)_v$
100	21.5	160	20.0
110	21.0	170	19.5
120	21.0	180	18.5
130	20.5	200	19.25
140	19.5	220	19.25
150	19.5		

(c) Volume of system = 3000 c.c.

Temperature, centigrade.	$k = \left(\frac{dp}{dT}\right)_v$	Temperature, centigrade.	$k = \left(\frac{dp}{dT}\right)_v$
30	31	70	28
40	31	80	31
50	29	90	32
60	27	100	29

Young says, "The values of $\left(\frac{dp}{dT}\right)_v$ are approximately but not completely constant. For volumes less than 4.6 c.c. the values of k increase with rising temperature, whilst at greater

volumes the values decrease. At still greater volumes they appear to be constant."

The general conclusion is that the Ramsay and Young equation is very nearly but not quite in agreement with the actual behaviour of liquid and gas systems.

II. THE EQUATION OF VAN DER WAALS.¹

This expression is wider in its scope than the first-quoted form of the Ramsay and Young equation, in that it is proposed as a substitute for the entire "perfect gas" law $p\bar{v} = RT$, and is to be applicable to actual gases and liquids.

It is written thus—

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = RT$$

Where a and b are regarded as constants characteristic of a given substance, but independent of temperature and volume. p , \bar{v} , R , T , have their usual significance. The above expression differs from the perfect gas law in that it contains two correction terms, $\frac{a}{\bar{v}^2}$ and b . The term $\frac{a}{\bar{v}^2}$ is introduced to take account of the attractive forces between the molecules.² These forces are extremely great when the system is liquid, and although decreasing rapidly with temperature rise and rarefaction, are still not negligible until the system is well above the critical point. The perfect gas law $p\bar{v} = RT$ assumes, of course, that there are no such *cohesive* forces operating between the molecules. In the interior of actual gases, vapours, and liquids, the cohesive forces which exist, say, upon a single molecule are mutually destructive because they are on the average exerted in all directions

¹ J. D. van der Waals, *Dissertation*, Leyden, 1873; *Die Kontinuität des gasförmigen und flüssigen Zustands*, Teile I. u. II., Leipzig, 1899. There is also an English translation of the German edition of 1881 in the *Physical Society Memoirs*.

² It will be remembered that in the introductory chapter it has been shown that the van der Waals' equation assumes the law of attraction to be the inverse fourth power of the distance between the molecules.

simultaneously. The existence of cohesion is shown when we consider a molecule near or at the surface. A molecule passing through the surface layer is retarded by the backwardly directed pull exerted upon it by the more interior molecules of the liquid, *i.e.* its impact, and therefore the pressure exerted by it is lessened owing to the cohesive forces. If such an imperfect gas or vapour exerts a pressure p against the walls of the containing vessel, the pressure which would be exerted by it if it obeyed Boyle's Law would be greater by a certain quantity π , *i.e.* the perfect gas under the same conditions would exert a pressure $(p + \pi)$. Van der Waals writes

$\pi = \frac{a}{v^2}$. His reason for doing so is roughly as follows. The attractive or cohesive force between two volume elements of liquid is proportional to the product of the masses of each element, that is, is proportional to the product of the densities, or if the elements are similar, is proportional to the square of the density, and therefore proportional to $\frac{1}{v^2}$, since v varies inversely as the density. Assuming the proportionality factor to be a constant a —which depends of course on the chemical nature of the liquid, vapour, or gas considered, but is assumed to be independent of the temperature and volume of the system—we can write—

$$\text{cohesive force} = \frac{a}{v^2}$$

and hence the true pressure which ought to be exerted by the system is $\left(p + \frac{a}{v^2}\right)$, where p is the *actual* pressure observed.

Again, it is clear that in the actual case the molecules of a system must occupy some space. Hence if a gas be compressed to a high degree, the actual volume v may no longer be great compared to the least possible volume which would be reached when the molecules were made to touch. This limiting volume is denoted by b —van der Waals has shown that b is four times the actual effective volume of the molecules.¹ The *compressible* volume, *i.e.* the *FREE* space is thus

¹ See footnote to page 17.

$(v - b)$, and this is the quantity which should appear in any modified form of Boyle's Law, for this law does not take account of any volume occupied by the molecules themselves. [It is more than likely that the law governing the actual compressibility of the molecules themselves is entirely different from a simple one such as that of Boyle.] When we allow, therefore, for the simultaneous modification of the pressure and volume terms, the corrected expression, put in the shape of a "Boyle's Law," takes the form—

$$\left(p + \frac{a}{v^2}\right)(v - b) = k$$

Now, if we simply make the *assumption* that the terms $\left(p + \frac{a}{v^2}\right)$ and $(v - b)$ should replace p and v in the general gas equation, we obtain—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

The above deduction of van der Waals' equation serves only to show the reasonableness of the modifications introduced. Van der Waals himself followed a more rigid method, starting from the Clausius virial.¹

Van der Waals' expression is a cubic equation in v , as is seen when it is rewritten in the form—

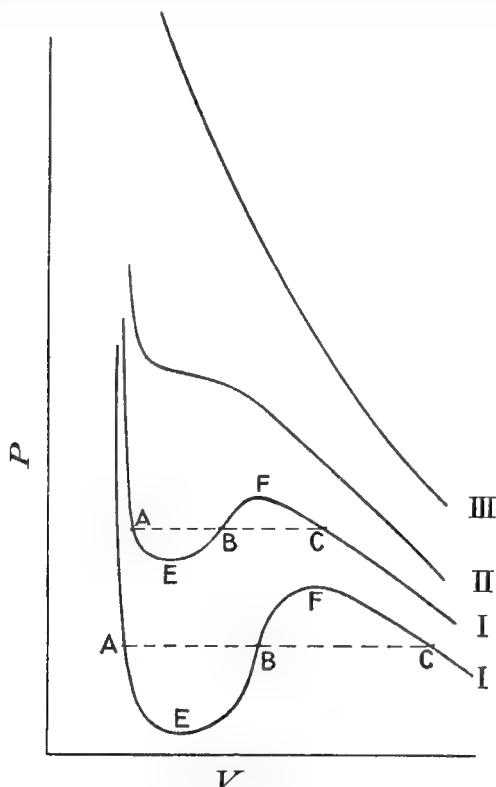
$$v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0$$

The equation has therefore three roots, *i.e.* three values of v for any given p and T , and further, all three roots may be real, or one real and two imaginary. The expression is therefore the equation of curves such as those shown in the diagram, Fig. 20.

When the roots are real and different, three different values for v (for a given p and T) are shown by the points A, B, and C

¹ The reader should consult van der Waals' monograph or Kuenen's *Die Zustandsgleichung*, in the "Wissenschaft" series.

in curve I on the p v diagram. When the p and T values are such that the three roots are real and identical, the curve given by the equation is represented by II. When there is one real root and two imaginary, the curve has the shape represented



VAN DER WAALS ISOTHERMALS.

FIG. 20.

by III. The resemblance between these curves and those suggested by James Thomson for the isothermals below, at, and above the critical point is very striking. The van der Waals equation carries out therefore this conception of the continuity of the liquid and gaseous states. It may also be pointed out that the equation predicts a similar continuity for

the solid and liquid states, though in view of Tammann's work¹ this is very doubtful. It cannot be too strongly emphasised that the van der Waals equation applies only to a *homogeneous* system, *i.e.* a system entirely liquid or entirely gaseous. It cannot be applied directly to the case of liquid in contact with saturated vapour, as this system is heterogeneous, *i.e.* two-phase. To make it apply to the passage from gas to liquid, or *vice versa*, we have to imagine the change to be continuous, that is, we have to imagine that, instead of the pressure remaining constant until liquefaction or vaporisation is complete, the pressure follows the curve AEBFC.

CALCULATION OF THE CRITICAL CONSTANTS WITH THE AID OF VAN DER WAALS' EQUATION.

First Method.—At the critical point the three roots of the equation are identical, *i.e.* there is only one value for v , namely, the critical volume v_c , which will satisfy the equation when the pressure and temperature have the critical values p_c and T_c . As already mentioned, v_c , p_c , and T_c are the critical constants of the substance under examination. It is possible to express them in terms of the van der Waals constants a and b in the following way:—

A cubic equation in v which possesses three identical roots may be written in the form—

$$(v - v_c)^3 = 0$$

where v_c is the root of the equation.

This expression when expanded in the ordinary way becomes—

$$v^3 - 3v_c v^2 + 3v_c^2 v - v_c^3 = 0$$

van der Waals' equation for the critical point being—

$$v^3 - \left(b + \frac{RT_c}{p_c}\right)v^2 + \frac{a}{p_c}v - \frac{ab}{p_c} = 0$$

¹ See G. Tammann's book, *Krystallisieren und Schmelzen*; see also Chwolson, *Lehrbuch der Physik*, vol. iii. pp. 583-4.

Now equating the coefficients of like powers of v in the two equations,¹ one obtains

$$3v_c = b + \frac{RT_c}{p_c} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$3v_c^2 = \frac{a}{p_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$v_c^3 = \frac{ab}{p_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From these equations one can obtain the following values for v_c , p_c , and T_c , namely :

$$v_c = 3b$$

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8}{27} \cdot \frac{a}{Rb}$$

and also

$$\frac{RT_c}{p_c v_c} = \frac{8}{3} = 2.67$$

If one determines, therefore, by experiment the pressures and volumes at various temperatures of the homogeneous liquid or gas, one can calculate a and b in the equation of state, and from these values the values of v_c , p_c , and T_c , or *vice versa*, a and b may be calculated by the above relations from the critical constants themselves.

Second Method.—The points E and F (Fig. 20) on the van der Waals isothermals below the critical point represent minima and maxima respectively. That is, at the point E the curve is such that $\frac{\partial p}{\partial v} = 0$, and $\frac{\partial^2 p}{\partial v^2}$ is positive. (Note that partial differentials are employed to denote that the temperature is constant.) Again, for the point F the curve is such that $\frac{\partial p}{\partial v} = 0$ and $\frac{\partial^2 p}{\partial v^2}$ is negative. At the critical temperature the points E and F coalesce. Hence for the critical isothermal we have the relations $\frac{\partial p}{\partial v} = 0$ and $\frac{\partial^2 p}{\partial v^2} = 0$. (Note that $\frac{\partial^2 p}{\partial v^2} = 0$

¹ See, for example, Hall and Knights' *Algebra*, Chap. 35.

means that the tangent to the curve at the point of inflexion is horizontal.¹) On rewriting van der Waals' equation in the form

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

one obtains on differentiating with respect to v , keeping T constant—

$$\frac{\partial p}{\partial v} = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3}$$

Further differentiation gives—

$$\frac{\partial^2 p}{\partial v^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4}$$

Hence at the critical point the following relations hold:—

$$\frac{-RT_c}{(v_c-b)^2} + \frac{2a}{v_c^3} = 0 \quad \text{and} \quad \frac{2RT_c}{(v_c-b)^3} - \frac{6a}{v_c^4} = 0$$

Dividing one expression by the other we obtain—

$$\frac{\frac{1}{2}(v_c-b)}{v_c} = \frac{\frac{1}{3}}{v_c} v_c$$

or

$$v_c = 3b \text{ as before.}$$

The values for p_c and T_c follow from this and take the form already given. This second method of examination has the advantage of being more general than the first, and is directly applicable to other equations of state.

CONNECTION BETWEEN VAN DER WAALS' EQUATION AND THE EQUATION OF RAMSAY AND YOUNG.

If we consider a homogeneous system—say a gas—which is kept at constant volume whilst undergoing pressure changes due to changes in temperature, the equation of van

¹ At higher temperatures there is still a point of inflexion, but $\frac{\partial^2 p}{\partial v^2}$ is no longer zero. Finally, at still higher temperatures the inflexion vanishes.

der Waals may be simplified thus. The term $\frac{a}{v^2}$ is now a constant, and may be denoted by c ; $(v - b)$ can also be regarded as a constant, say c_1 , so that the equation becomes—

$$(p + c)c_1 = RT$$

or, denoting $\frac{R}{c_1}$ by k ,

$$\begin{aligned} p + c &= kT \\ p &= kT - c \end{aligned}$$

or

which is the Ramsay-Young equation. The van der Waals equation will therefore give rise to the same type of isochores as those given by the Ramsay-Young expression. The connection between the equations may also be observed if we write the Ramsay-Young expression in the form—

$$p = Tf(v) - F(v)$$

and the van der Waals expression in the form—

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

They are identical on the assumption that—

$$f(v) = \frac{R}{v - b} \quad \text{and} \quad F(v) = \frac{a}{v^2}$$

Van der Waals' equation is therefore a special case of the general Ramsay-Young equation for systems at constant volume.

APPLICATION OF VAN DER WAALS' EQUATION TO SOME ACTUAL CASES.

Van der Waals himself gives the following calculations based on Andrews' data for carbon dioxide. The object is to see if a and b are really constant. The two terms occur, of course, simultaneously, and if there be variation in one it will not be possible to eliminate the effect from the other. Employing the same units for p and v as those of Andrews,

van der Waals has calculated a to be 0.008704 for CO_2 gas. Taking this to be correct, the following table indicates the values of b calculated from the equation in the case of CO_2 :—

Temperature 13.1° C.		Temperature 21.5° C.	
v .	b .	v .	b .
CO_2 entirely gaseous	0.013764	0.016044	0.00241
	0.013036	—	—
	0.012933	—	—
CO_2 entirely liquid	0.0022647	0.002935	0.001924
	0.0022234	0.0024526	0.001734
	0.0021822	0.0024288	0.001719
	0.0020937	—	—
	0.0020527	—	—
	0.001663		
	0.001643		
	0.001627		
	0.001585		
	0.001565		

Temperature 35.5° C. (above the critical point. System therefore entirely gaseous).

v .	b .	v .	b .
0.01367	0.0025	0.007016	0.0025
0.012716	0.0025	0.00496	0.00234
0.01173	0.0027	0.00321	0.0020
0.0106	0.0025	0.003026	0.00195
0.00955	0.00244	0.00275	0.00184
0.00837	0.00254	0.002629	0.001798

It will be seen from the above data that b is *not* constant. It decreases as v decreases, *perhaps* due to a slight compressibility on the part of the molecules themselves, though this can hardly be regarded as the whole cause. There is evidence also—although not shown clearly by the data quoted—that b increases slightly with rise in temperature. The data show, however, that on the whole the equation expresses with considerable approximation the behaviour of gaseous and liquid systems. The degree of applicability will be more clearly realised when it is remembered that although the term a/v^2 , which is the cohesive or “internal”—or “intrinsic”—or “molecular”—pressure term, varies from a few atmospheres

in the gaseous state to over 1000 atmospheres¹ for the liquid state in the case of carbon dioxide, yet the value of b varies within moderate limits.

It will be of interest to see how far the equation applies to another case, namely, ethylene. From the values of v_c , p_c and T_c experimentally obtained, van der Waals calculated a to be 0.00786 and b to be 0.00224. Assuming these to be constants, the following values of the products (pv) were calculated by Baynes (*Nature*, 22, 186, 1880):—

ETHYLENE AT 20° C.

p in atmospheres.	(pv) observed by Amagat.		(pv) calculated from van der Waals' equation.
1	1000 (in arbitrary units)		1000
31.58	914	„ „	895
72.9	416	„ „	387
84.16	399	„ „	392
110.5	454	„ „	456
176.01	643	„ „	642
233.58	807	„ „	805
282.21	941	„ „	940
329.14	1067	„ „	1067
398.71	1248	„ „	1254

The two columns of figures agree fairly well. A more complete examination of the equation has shown, however, that in no case can a or b be regarded as absolutely constant, and hence, although the van der Waals equation gives an approximate solution, it is recognised that its applicability is not rigid. These conclusions appear more clearly from considerations such as the following:—

¹ APPROXIMATE VALUES OF THE INTERNAL PRESSURE OF LIQUIDS.

The following are the values obtained by van der Waals in the case of a few *liquids* at 0° C. approximately:—

Ethyl ether, 1300 atmospheres.

Ethyl alcohol, 2100 „

Carbon disulphide, 2900 atmospheres.

Water, 10500 atmospheres.

For further values, see a paper by W. C. McC. Lewis, *Trans. Faraday Soc.*, 1911; and *Phil. Mag.*, July, 1914.

COMPARISON OF THE RATIO OF RT TO $p_c v_c$ AT THE CRITICAL POINT AS GIVEN BY THE EQUATION AND THAT ACTUALLY OBSERVED.

If one substitutes in the ratio $\frac{RT}{p_c v_c}$ the values of the critical constants p_c , v_c and T_c , as given by the van der Waals equation, it is found that the ratio simply reduces to the quantity $\frac{8}{3}$ or 2.67, which should therefore be the same for *all* substances. It will be seen that the above ratio is identical with the ratio between the value of $p_c v_c$ for a perfect gas (since this is RT) and the value of $p_c v_c$ for an actual gas. (In other words, 2.67 is the ratio of the density of a gas obeying van der Waals' equation to that of a perfect gas at the same (critical) temperature and pressure.)

The following data (selected mainly from S. Young's paper, *Proc. Roy. Dub. Soc.*, **12**, 374, 1910) show the experimentally determined values of the ratio $\frac{RT_c}{p_c v_c}$ for a number of substances.

Substance.	$\frac{RT_c}{p_c v_c}$
Helium	3.13 ¹
Argon	3.283 ¹
Xenon	3.605 ²
Oxygen	3.346 ³
Ethylene	3.42
<i>n.</i> pentane	3.766
<i>n.</i> hexane	3.831
<i>n.</i> heptane	3.854
<i>n.</i> octane	3.865
Isopentane	3.735
Hexamethylene	3.706
Benzene	3.755
Fluorobenzene	3.796
Chlorobenzene	3.776
Bromobenzene	3.809
Iodobenzene	3.780

¹ Onnes, *Proc. Roy. Acad. Amsterdam*, 1911.

² Patterson, Cripps and R. Whytlaw-Gray, *Proc. Roy. Soc.*, A. **86**, 579, 1912.

³ Onnes, *Proc. Roy. Acad. Amsterdam*, 1911.

Substance.	$\frac{RT_c}{p_c v_c}$
Carbon tetrachloride	3·680
Zinc chloride	3·740
Ethyl ether	3·813
Methyl formate	3·922
Ethyl formate	3·895
Methyl acetate	3·943
Ethyl acetate	3·949
Methyl butyrate	3·903
Carbon dioxide	3·620
Sulphur dioxide	3·830
<i>" Abnormal Substances."</i>	
Methyl alcohol	4·559
Ethyl alcohol	4·026
Propyl alcohol	3·998
Acetic acid	4·992

It will be observed that the experimentally found value for the ratio $\frac{RT_c}{p_c v_c}$ is nearly a constant for a large number of substances as van der Waals' equation predicts, but the actual numerical value is approximately $\frac{4}{3}$ times as great as the theoretical value (2·67). This is of course a very serious discrepancy, and up to the present no satisfactory explanation of it is forthcoming. It may be pointed out that the mean experimental value indicates that the actual density for the above "normal" substances at their critical points is approximately 3·7 times the density of a perfect gas. Note that the monatomic gases, argon and xenon—which from their simple structure might be expected to approximate most closely to van der Waals' equation—show much the same discrepancy as other substances whose molecules are much more complex.

BEHAVIOUR OF MATTER AT EXTREMELY HIGH PRESSURES.

According to van der Waals' equation the critical volume $v_c = 3b$ or $b = \frac{v_c}{3}$. If a substance be compressed a limit is theoretically reached when the volume becomes equal to b , that is, to $\frac{v_c}{3}$. It has been found, however, that in the actual

cases the limiting volume is approximately $\frac{v_c}{4}$, i.e. matter is more compressible than is predicted by the equation. This "found" limit is obtained by extrapolation of the Cailletet-Mathias mean density line to the temperature $T = 0^\circ$ absolute, at which point the density of the vapour is zero and the actual density of the liquid is double the value given by the mean density line. In this way Guldberg, and later D. Berthelot (*Archives Néerlandaises*, (2) 5, 446, 1900) found the following values for the limiting specific volumes of various substances:—

O ₂	Cl ₂	CO ₂	SO ₂	C ₂ H ₄
0·278 v_c	0·282 v_c	0·269 v_c	0·243 v_c	0·243 v_c
	CCl ₄	C ₄ H ₁₀ O	C ₆ H ₆	
	0·260 v_c	0·255 v_c	0·258 v_c	

The mean of these values is 0·26 v_c , the value given by van der Waals' equation being 0·33 v_c .

THE VARIATION OF THE PRODUCT $p v$ WITH p FROM THE STANDPOINT OF VAN DER WAALS' EQUATION.

In the diagrams (Figs. 10 to 14) it has been shown that the isothermal variation of the product $p v$ with p passes through a minimum, except in the case of hydrogen, at ordinary temperatures. The position of the minimum alters with the temperature, a series of such minima in the case of CO₂ being represented in Fig. 14 by the longer dotted line. It will be observed that this is parabolic in shape, and may be extrapolated on the upper side until it cuts the $p v$ axis. This simply means that at and above a certain temperature the isothermal $p v$, p curves on the diagram will be similar to those of hydrogen at ordinary temperatures, since the minimum is now shifted over to the axis. Let us consider this state of things, namely, that the system is just at the temperature at which the minimum point is on the $p v$ axis. For any of the minimum points indicated by the dotted line (Fig. 14) the following relation necessarily holds:—

$$\frac{\partial(pv)}{\partial p} = 0$$

Now, according to van der Waals—

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

and therefore

$$pv = \frac{RTv}{v-b} - \frac{a}{v}$$

Hence

$$\frac{\partial(pv)}{\partial p} = \left\{ \frac{RT(v-b-v)}{(v-b)^2} + \frac{a}{v^2} \right\} \frac{\partial v}{\partial p} = \left\{ \frac{-bRT}{(v-b)^2} + \frac{a}{v^2} \right\} \frac{\partial v}{\partial p}$$

It is not necessary to work out the expression for $\frac{\partial v}{\partial p}$. It is clear that it will have a real value, not zero. The above expression for $\frac{\partial(pv)}{\partial p}$ will, therefore, be zero, *i.e.* there will be a minimum point on the curve when—

$$\frac{(v-b)^2}{v^2} = \frac{b}{a} RT$$

This relation holds good as a criterion of any of the minima. Now consider the special case of the minimum point being just on the pv axis. Suppose the temperature is T_1 . Since $p=0$, $v=\infty$. Hence the above relation becomes—

$$\frac{b}{a} RT_1 = 1, \text{ or } RT_1 = \frac{a}{b}$$

Now if we write a and b in terms of the critical temperature of the gas, we have the following equations:—

$$RT_c = \frac{8}{27} \frac{a}{b}$$

and therefore—

$$T_1 = \frac{27}{8} T_c = 3.375 T_c$$

According to van der Waals' equation, therefore, the temperature, at which the minimum value of pv on the $(pv)p$ sets of curves is found just on the pv axis, should be 3.375 times the critical temperature of the gas—no matter what the gas may be. Let us compare this with experiment. Employing the data of Amagat in the case of CO_2 , the value for T_1 is

found to be 636°C. , or 909°abs. , whilst the critical temperature is 304°abs. The ratio is 2.98. Other gases have been examined (Leduc and Sacerdote, *Compt. Rend.*, 124, 285, 1897), and the ratio in these cases is also approximately 2.98. We see once more, therefore, that the van der Waals' equation, whilst correctly predicting the general behaviour and relations, breaks down in the quantitative conclusions.

THE PRINCIPLE OF CORRESPONDING STATES.

Consider the van der Waals equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

for any given homogeneous substance—either liquid or gas. Let us express the p , v , and T as multiples or submultiples of the critical values p_c , v_c , and T_c ; that is, let us write—

$$\begin{array}{lll} \text{The actual pressure } p & \text{as } \pi p_c \\ \text{,, volume } v & \text{,, } \phi v_c \\ \text{,, temperature } T & \text{,, } \theta T_c \end{array}$$

Substituting these values in the above equation, we obtain—

$$\left(\pi p_c + \frac{a}{\phi^2 v_c^2}\right)(\phi v_c - b) = R\theta T_c$$

If we write now the values of a , b , and R likewise in terms of the critical constants (p. 99), the equation takes the form—

$$\left(\pi p_c + \frac{3p_c v_c^2}{\phi^2 v_c^2}\right)\left(\phi v_c - \frac{v_c}{3}\right) = \frac{8}{3} \frac{p_c v_c}{T_c} \cdot \theta T_c$$

which reduces to

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$$

an expression which does not contain the characteristic constants a or b for any particular substance. This equation, written in conformity with the recommendations of the "International Commission" takes the form

$$\left(p_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r$$

This equation is known as the *reduced equation of state*, and should apply equally to all substances. In other words, if we consider any two substances whatsoever, either in the liquid or in the gaseous form, and suppose that we choose the temperature of each substance so that each temperature is the same fraction of the respective critical temperature, and if we bring the pressure of each substance to the same fraction of the respective critical pressure, then it will be found that the volume of each substance is the same fraction of the respective critical volume for each.

When the pressures exerted by any two substances are the same fraction of the respective critical pressures, the substances are said to be at *corresponding pressures*. An analogous definition holds for the terms *corresponding temperature* and *corresponding volume*. When any two of the variables p , v , T are fixed for a series of substances in such a way that the values are corresponding values, then, as shown above, the third variable will also be found to correspond for the various substances, and the substances are said to be in *corresponding states*.

We may now consider some experimental data collected by S. Young for the purpose of investigating this principle. The systems were selected so that the ratio π or p_r of the actual pressures of the various substances to the respective critical pressures is the same for all, and has the value 0.08846. At the same time, the temperatures were chosen so that the ratio θ or T_r of the absolute temperatures to the respective critical temperatures was the same for all, namely, 0.73 to 0.74. The following table shows the value of ϕ or v_r , the ratio of the actual specific volumes to the respective critical volumes. The substances are all examined under *corresponding* conditions with respect to temperature and pressure, and, therefore, if the principle of corresponding states is true, the observed volumes should likewise be at corresponding values, *i.e.* v_r should be the same for all. It will be observed that the temperatures and pressures happen to be so chosen that the substances can exist both in the liquid and in the vapour state. There are, therefore, two series of specific volumes to be taken into

account, namely v_{liquid} and v_{gas} , corresponding to the end points of the horizontal line in the $p v$ diagram. According as we consider the homogeneous liquid or homogeneous gaseous state, there is a different numerical value to be assigned to the ratio of the actual to the critical volume for such substance. There are, therefore, two columns of figures in the table. The principle of corresponding states would, however, lead us to expect that if we compare liquids throughout or gases throughout the values of v_r should be the same for all substances, since each system has previously been brought to the same p_r and T_r .

SUBSTANCES IN CORRESPONDING STATES (data taken from portion of table in Young's *Stoichiometry*, p. 219).

$$p_r = 0.08846$$

$$T_r = 0.73 \text{ to } 0.74$$

Substance.	$\frac{v_{\text{liquid}}}{v_c} = v_{r1}$	$\frac{v_{\text{gas}}}{v_c} = v_{r2}$
Benzene	0.4065	28.3
Isopentane . . .	0.4085	27.7
<i>n.</i> Pentane . . .	0.4061	28.4
<i>n.</i> Hexane	0.4055	29.1
Fluorbenzene . .	0.4067	28.4
Chlorbenzene . .	0.4028	28.5
Carbon tetrachloride	0.4078	27.45
Ethyl ether . . .	0.4030	28.3
Methyl formate . .	0.4001	29.3
Ethyl formate . .	0.4003	29.6
$T_r =$ { Methyl acetate . .	0.3989	30.15
0.77 { Acetic acid	0.4100	25.4
ap- { Methyl alcohol . .	0.3973 approx.	34.35
proxi- { Propyl alcohol . .	0.4002 ,,	30.85
mately. { Ethyl alcohol . . .	0.4061 ,,	32.15

The principle of corresponding states is thus in agreement with experience, although it is noticeable that the correspondence is better the more closely the substances are related chemically.

It is of importance to notice that the conclusion to which one has come on the basis of the van der Waals equation in regard to the existence of corresponding states does not necessarily stand or fall with the applicability or inapplicability of the equation itself. It is quite conceivable that other equations would

also predict the existence of corresponding states. It will be done, in fact, by any equation containing three constants, *i.e.* as many constants as there are variables, p , T , and v . In van der Waals' equation the three constants are a , b , and R . The principle of corresponding states would not be predicted by an equation such as that of Clausius, which will be considered next, since this contains four constants, a , b , c , and R , unless some connection exists between a pair of these constants themselves.

Two methods (due to Amagat and Raveau respectively) of testing the reduced equation of state are given by Kuenen (*Die Zustandsgleichung*, pp. 84-86), also Young's *Stoichiometry*, pp. 215 *seq.* It has been found that the equation corresponds very closely to experiment in regions well above the critical point, but shows considerable discrepancies in the neighbourhood of this point.

III. THE EQUATION OF CLAUSIUS.

We have seen that the terms a and b in van der Waals' formula are not absolute constants, since they vary with temperature and volume. Clausius (*Wied. Ann.* 9, 337, 1880) suggested, therefore, that the term a/v^2 should be replaced by the term $\frac{a}{(v+c)^2} \cdot \frac{1}{T}$. In this expression it is assumed that the cohesive force varies inversely as the absolute temperature. c is a constant, characteristic of the substance under examination. The Clausius equation is, therefore—

$$\left\{ p + \frac{a}{T(v+c)^2} \right\} (v-b) = RT$$

We now proceed to test the applicability of this equation.

By applying the usual criteria for the critical point, namely, that $\frac{\partial p}{\partial v} = 0$, and $\frac{\partial^2 p}{\partial v^2} = 0$, one finds the relations—

$$\frac{-RT_c}{(v_c-b)^2} + \frac{2a}{T_c(v_c+c)^3} = 0$$

and

$$\frac{2RT_c^2}{(v_c-b)^3} - \frac{6a}{T_c(v_c+c)^4} = 0$$

From these one deduces the following values for the critical constants :—

$$\begin{aligned} v_c &= 3b + 2c \\ \frac{p_c}{RT_c} &= \frac{1}{8} \frac{1}{b + c} \\ RT_c^2 &= \frac{8}{27} \frac{a}{b + c} \end{aligned}$$

It will be observed that the Clausius equations contain four constants a , b , c and R . The principle of corresponding states (which is borne out fairly completely by experience) requires, as we have seen, a *three*-constant formula. In order to be able to predict the principle of "correspondence" from the Clausius' equation it is necessary to assume that c is a function of b , and this function must be the same for all substances. Thus, according to the principle, the expression $\frac{RT_c}{p_c v_c}$ should be the same for all substances. From the above relations it will be seen that—

$$\frac{RT_c}{p_c v_c} = \frac{8(b + c)}{3b + 2c}$$

and this can only be constant when b and c are proportional to one another. Thus, if $c = kb$, then

$$\frac{RT_c}{p_c v_c} = \frac{8(1 + k)}{3 + 2k}$$

where k is supposed to have the same value for all substances—a pure assumption.

Further, let us apply Clausius' equation to the pv , p diagram. The temperature which has been denoted by T_1 , namely, that at which the minimum point of the pv curve lies just on the pv axis (*i.e.* $v = \infty$, $p = 0$), was defined according to the van der Waals equation by the relation $RT_1 = \frac{a}{b}$. The

Clausius equation gives the relation $RT_1^2 = \frac{a}{b}$. Substituting

the values of a and b obtained from the critical data, viz. :—

$$RT_c^2 = \frac{8}{27} \frac{a}{b+c} = \frac{8}{27} \frac{a}{b(1+k)}$$

we obtain— $T_1^2 = T_c^2 \cdot \frac{27}{8}(1+k)$

or $T_1 = T_c \sqrt{\frac{27}{8}(1+k)}$

Now, we saw by *experiment* that $T_1 = 2.98T_c$ on the average; and in order to obtain this numerical relation from the above expression it is necessary to write $k = 1.54$.

Employing this value for k we find that—

$$\frac{RT_c}{p_c v_c} = \frac{8(1+k)}{3+2k} = 3.34$$

This value is nearer the actual mean experimental value, 3.375, than the value given by van der Waals' equation (2.67), but it is still too low. That is, the Clausius equation is also not exact. The equation has been found, further, to break down when examined in other directions, and for these reasons we need not further consider it, especially as it has the disadvantage of containing one arbitrary constant in addition to those analogous to the van der Waals constants without possessing a correspondingly greater accuracy of applicability.

IV. THE EQUATION OF DIETERICI.

C. Dieterici (*Ann. der Physik*, [4] 5, 51, 1901) has suggested the following expression :—

$$p(v-b) = RTe^{-\frac{A}{RTv}}$$

where e is the base of natural logarithms, b has the same significance as in van der Waals' equation, and is treated in the first instance as a constant. The term A is a constant characteristic of the cohesion pressure. The general considerations upon which the above expression is based may be briefly stated.

In the interior of a gas whose molecules possess cohesive force it may be assumed that since the cohesion is effective in all directions simultaneously, the translatory movements of the molecules will not be affected by it, and the pressure P_1 in the interior would be accurately given on the basis of the kinetic theory of gases. The actual pressure exerted upon the boundary or walls of the enclosing vessel will be smaller than P_1 , because of the effective pull towards the interior exerted upon the molecules at the surface. On these grounds, therefore, we see that (1) the *number* of molecules which reach the boundary per second is smaller than those reaching an imaginary plane in the interior, because some of the molecules will possess too little velocity to reach the boundary at all, *i.e.* they will possess too little kinetic energy to overcome the backward pull; and (2) those molecules which do reach the boundary have lost some of their kinetic energy in overcoming the backward pull, and will therefore possess less momentum, and hence exert a smaller pressure than the same number would exert in the interior. Hence, if one denotes by A the work—reckoned per unit mass of the gas—done against the cohesive pull, the actual pressure p exerted by the gas at the boundary will be given by the expression—

$$p = P_1 e^{-\frac{A}{RT}}$$

But $P_1 = \frac{RT}{v - b}$, which is the ordinary gas equation, in which, however, the molecules are not regarded as points but as occupying a certain volume, such modification being represented by the b term. Substituting this relation in the first equation, one obtains—

$$p = \frac{RT}{v - b} e^{-\frac{A}{RT}}$$

or
$$\frac{A}{RT} = \log_e \frac{RT}{p(v - b)}$$

Dieterici found, however, that the values thus given for A varied with the volume in the sense that A diminished

as v increased. He therefore replaced the term $\frac{A}{RT}$ by $\frac{A}{RTv}$, thus obtaining the equation—

$$p = \frac{RT}{v-b} \cdot e^{-\frac{A}{RTv}}$$

Dieterici showed that this equation will yield the following results: (1) A maximum and minimum value for p as in the case of isothermals on the pv diagram below the critical point (compare the theoretical isothermals of van der Waals, Fig. 20, or of James Thomson, Fig. 18); (2) that at a certain temperature the equation gives a pressure curve on the pv diagram which contains a point of inflection, *i.e.* the critical isothermal; and (3) that at higher temperature the curves for p show neither a maximum nor minimum,¹ and and thus correspond to the actual shape of isothermals above the critical point. These conclusions can be shown as follows:—Let us differentiate the expression with respect to v , temperature being kept constant and b being likewise regarded as a constant. The condition for a maximum or minimum point on the pv curve is that $\frac{\partial p}{\partial v} = 0$, that is,

writing $\frac{A}{RT}$ as a constant c , one obtains the relation—

$$\frac{-RT}{(v-b)^2} \cdot e^{-\frac{c}{v}} + \frac{RT}{v-b} e^{-\frac{c}{v}} \times \frac{c}{v^2} = 0$$

whence

$$\frac{c}{v^2} = \frac{1}{v-b}$$

or

$$v = \frac{c}{2} \left(1 \pm \sqrt{1 - \frac{4b}{c}} \right)$$

When c is greater than $4b$ there are two values of v at which $\frac{\partial p}{\partial v} = 0$, that is, at which p has either a maximum or minimum value. This corresponds to the James Thomson isothermals

¹ The curves may still show an inflexion point, but $\frac{\partial^2 p}{\partial v^2}$ is only zero at the critical point, *i.e.* the tangent is horizontal only at T_c .

below the critical point. When c is equal to $4b$ the roots of the equation are identical. This corresponds to the critical isothermal. When c is less than $4b$ the roots are imaginary. In other words, there is no real value of v for which $\frac{\partial p}{\partial v} = 0$, *i.e.* for which p is a maximum or minimum. This is the case for isothermals above the critical point. We thus see that, qualitatively at least, this equation is in agreement with the general idea of continuity of state.

Further, it will be observed that the equation contains three constants. It is therefore in agreement with the principle of corresponding states.

Now let us calculate the values of the critical constants, T_c , p_c , v_c , in terms of the Dieterici constants. As we have already seen, the criteria of the critical point are represented by the relations—

$$\frac{\partial p}{\partial v} = 0, \text{ and } \frac{\partial^2 p}{\partial v^2} = 0$$

Carrying out this differentiation of the Dieterici expression, one obtains two equations by means of which the following relations may be deduced:—

$$\begin{aligned} v_c &= 2b \\ RT_c &= \frac{A}{4b} \\ p_c &= \frac{A}{4b^2} \cdot e^{-2} \end{aligned}$$

From these it follows at once that—

$$\frac{RT_c}{p_c v_c} = \frac{1}{2} e^2 = 3.695$$

a value which is in very good agreement with the average experimental figures, pp. 104, 105. On this particular point, therefore, the Dieterici equation is in much closer agreement with experiment than is the equation of van der Waals.

For the case of the critical isothermal, the Dieterici equation can be written—

$$p = \frac{RT_c}{v - b} e^{-\frac{A}{RT_c v}}$$

and on substituting the critical constants in place of A and b the equation becomes—

$$p = \frac{RT_c}{v - \frac{1}{2}v_c} \cdot e^{-\frac{2v_c}{v}}$$

To show the agreement between theory and experiment, this expression has been applied to the calculation of the critical isothermal in the case of isopentane.

CRITICAL ISOTHERMAL OF ISOPENTANE.

$$T_c = 460.8$$

$$v_c = 4.266 \text{ c.c.}$$

v in c.c.	p calculated (mm. mercury).	p observed (mm. mercury).	v in c.c.	p calculated (mm. mercury).	p observed (mm. mercury).
2.4	42,730	49,080	8	23,400	23,710
2.5	35,810	40,560	10	21,590	22,040
2.6	32,090	34,980	12	19,850	20,300
2.8	28,390	28,940	15	17,540	17,980
3.0	26,780	26,460	20	14,560	14,840
3.2	26,000	25,490	30	10,770	10,950
3.6	25,420	25,050	40	8,508	8,570
4.0	25,320	25,020	50	7,025	7,068
4.3	25,300	25,005	60	5,978	6,001
4.6	25,300	25,000	80	4,604	4,614
5.0	25,240	24,940	90	4,127	4,132
6.0	24,880	24,840	100	3,740	3,750

Except in the case of the smallest volumes (high pressure region) the agreement between calculation and experiment is within 1 to 2 per cent. Dieterici concludes that the discrepancies which do exist are due to the fact that b is not quite constant, but is a function of v .

The most serious drawback, however, to Dieterici's equation is the fact that it yields the relation $v_c = 2b$. When p is infinitely great the limiting volume becomes identical with b , and therefore, according to Dieterici, identical with $\frac{1}{2}v_c$. It has been already shown experimentally, however (p. 106), that the limiting volume is more nearly $\frac{1}{4}v_c$. Dieterici's equation shows therefore an even greater discrepancy as regards this quantity than does the equation of van der Waals, according to which the limiting volume is $\frac{1}{3}v_c$.

The equation of Dieterici may be put in a somewhat different and at the same time more general form if the term T be raised to the n th power, n being characteristic of the substance under investigation. The expression is then—

$$p = \frac{RT}{v-b} e^{-\frac{a}{T^n v}}$$

By differentiation it follows that—

$$\frac{\partial \log p}{\partial v} = \frac{1}{p} \frac{\partial p}{\partial v} = -\frac{1}{v-b} + \frac{a}{T^n v^2}$$

and
$$\frac{\partial}{\partial v} \left(\frac{\partial \log p}{\partial v} \right) = \frac{1}{p} \frac{\partial^2 p}{\partial v^2} - \frac{1}{p^2} \left(\frac{\partial p}{\partial v} \right)^2 = \frac{1}{(v-b)^2} - \frac{2a}{T^n v^3}$$

At the critical point each of these expressions is zero; that is—

$$\frac{1}{v_c - b} = \frac{a}{T_c^n v_c^2} \quad \text{and} \quad \frac{1}{(v_c - b)^2} = \frac{2a}{T_c^n v_c^3}$$

Whence
$$v_c = 2b$$

$$T_c^n = \frac{a}{b^4}$$

$$p_c = \frac{R \left(\frac{a}{4b} \right)^{\frac{1}{n}} e^{-2}}{b}$$

and
$$\frac{RT_c}{p_c v_c} = \frac{(v_c - b)}{v_c} e^2 = \frac{1}{2} e^2 = 3.69 \text{ as before.}$$

THE VARIATION OF pv WITH p FROM THE STANDPOINT OF THE GENERAL DIETERICI EQUATION.

The general Dieterici equation yields the following expression for pv :—

$$pv = \frac{RTv}{v-b} e^{-\frac{a}{T^n v}}$$

Hence
$$\log(pv) = \log RT + \log v - \log(v-b) - \frac{a}{T^n v}$$

or
$$\frac{1}{pv} \frac{\partial(pv)}{\partial p} = \left(\frac{1}{v} - \frac{1}{v-b} + \frac{a}{T^n v^2} \right) \frac{\partial v}{\partial p}$$

The minimum point for each isothermal on the p v , p diagram is given by the relation—

$$\frac{1}{pv} \frac{\partial}{\partial p}(pv) = 0$$

and since $\frac{\partial v}{\partial p}$ is not zero, it follows that this condition is satisfied when—

$$\frac{1}{v} - \frac{1}{v-b} + \frac{a}{T^n v^2} = 0$$

or

$$T^n = \frac{a}{b} \left(1 - \frac{b}{v} \right)$$

For the particular case in which the minimum of the curve lies just on the p v axis (*i.e.* $p=0$ and $v=\infty$), the temperature T_1 is given by the last equation in the form—

$$T_1^n = \frac{a}{b}$$

On substituting the critical constants for a and b , one finds

$$\frac{T_1^n}{T_c^n} = 4 \quad \text{or} \quad T_1 = T_c \sqrt[4]{4}$$

Now it has been pointed out, in discussing the van der Waals equation, that the experimental value of the ratio $\frac{T_1}{T_c}$ is 2.98 for a number of gases (whether this is really a constant or not is still undecided). To make the above relation conform to this it is necessary to write $\sqrt[4]{4} = 2.98$, whence $n = 1.27$.

If we regard this number as a constant *independent of the nature of the gas*, the general form of the Dieterici equation is likewise a three-constant one, and therefore the number of constants (a , b , and R) is equal to the number of variables (p , v , and T), and a "reduced equation" can be written down containing quantities independent of the nature of any particular substance, and therefore in agreement with the principle of corresponding states. It will be observed that the first equation of Dieterici is obviously a three-constant one.

Many other equations of state have been proposed, but the brief survey given of those of Ramsay and Young, van der Waals, Clausius, and Dieterici respectively is sufficient to indicate the nature of the problem and the limitations exhibited by each. No equation altogether satisfactory has yet been proposed; that is, in no case are the "constants" quite independent of temperature and volume. We shall return to these equations later from the standpoint of thermodynamics (Part II. (Vol. II.), Chap. III.). In the meantime we may conclude this chapter by a short account of the attempts made to deal with heterogeneous systems containing liquid in contact with saturated vapour, these being characterised by the fact that on compression or rarefaction the volume undergoes considerable change while the pressure remains constant, until in fact one or other of the phases has entirely disappeared. As already pointed out, this horizontal portion of the experimental isothermals (below the critical point) is not taken account of by equations of state, owing to the fact that the actual isothermals are discontinuous whilst the equations refer only to continuous changes.

EMPIRICAL RELATIONS IN CONNECTION WITH SATURATED VAPOURS.

The Ramsay-Young Boiling Point Law.—If we compare two closely related substances A and B, *e.g.* methyl acetate and ethyl acetate, under equal pressures, it will be found that the following relation holds good, namely:—

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} = \text{a constant}$$

where T_A and T_B are the absolute boiling points of A and B under a given pressure the same for both, and T'_A and T'_B are also the absolute boiling points under a different pressure, likewise the same for both.

A more accurate expression is—

$$\frac{T'_A}{T'_B} = \frac{T_A}{T_B} + c(T'_A - T_A)$$

This relation was first discovered by Ramsay and Young in 1885 (*Phil. Mag.*, [5] 20, 515, 1885; *ibid.*, 21, 33; 22, 37, 1886). In many cases c is practically zero, and the simpler expression holds good. The relation is a valid one from very low pressures up to the critical. Its utility is evident, in that, if the boiling points of a given substance are known over a wide pressure range, and if a few similar determinations be made in the case of a second substance, the remaining values of the boiling points of the second substance may be calculated over the pressure range for which the first substance was measured. The constancy or lack of constancy of c may also be used as a test of normality or abnormality in connection with the molecular state of liquids. For the connection between the Ramsay-Young Boiling Point Law and Bertrand's vapour-pressure formula, the reader is referred to the paper by A. W. Porter (*Phil. Mag.*, [6] 13, p. 724, 1907).

The Vapour Pressure Formulæ of Biot, Rankine, Hertz, Bertrand, and van der Waals.—To describe the variation of the pressure of saturated vapour (in contact with a liquid) with temperature, Biot proposed the following :—

$$\log p = a + ba^t + c\beta^t$$

Rankine later suggested the expression—

$$\log p = a - \frac{\beta}{T} - \frac{\gamma}{T^2}$$

where p is the vapour pressure, α , β , and γ are empirical constants to be obtained by experiment, and T is the absolute temperature to which p refers. This type of formula is in frequent use, as it reproduces experimental values fairly well. A closer approximation may be obtained, however, by employing the relation due to Bertrand, namely—

$$p = G \left(\frac{T - a}{T} \right)^n \quad \text{or} \quad p^{\frac{1}{n}} = g \left(1 - \frac{a}{T} \right)$$

G , g , a and n being likewise empirical constants.

Recently, however, considerable attention has been drawn chiefly by the work of Nernst and others in connection with the new theorem of heat (Part II. (Vol. II.), Chap. XII.) to the expression first proposed by Hertz (*Wied. Ann.*, 17, 199, 1882), viz.—

$$\log p = k_1 - k_2 \log T - \frac{k_3}{T}$$

This has been applied, for example, by Knudsen to the case of the vapour pressure of mercury (*Ann. der Physik.*, [4] 29, 179, 1909), in connection with his new method of determination of very small¹ vapour pressures. The expression in this case becomes—

$$\log p = 10.5724 - 0.847 \log T - \frac{3342.26}{T}$$

In the following table are given some of the values obtained by Knudsen as well as by Morley, Hertz, Ramsay and Young, Smith and Menzies,² and others.

VAPOUR PRESSURE OF MERCURY.

Temperature, degrees centigrade.	Pressure observed in mm. mercury.	Observer.	Pressure calculated (Knudsen).	Pressure calculated (Smith and Menzies).
0°	0.0001846	Knudsen	—	0.000207 mm.
7.1	0.0003667	„	0.0003691	
16	0.0010	Morley	0.00084	
30	0.0027	„	0.00275	
50	0.0113	„	0.0126	0.01340
70	0.0404	„	0.0480	
89.4	0.16	Hertz	0.15	
117	0.71	„	0.64	0.2793 at 100°
154.2	3.49	„	3.32	2.811 at 150°
165.8	5.52	„	5.22	
190.4	12.89	„	12.65	
222.15	34.40	Ramsay &	34.70	17.22 at 200°
280.20	157.15	Young	161.1	74.10 at 250°
357.48	768.4 to 766.76	„	794	304.69 at 300°
447	2896.9	„	3240	1566.1 at 400°
570	15 to 17 atmos.	Caillietet	17.7 atmos.	3245.0 at 450°
650	34 „	Colardeau	36 „	
720	59 „	and Riviere	61 „	
770	80 „	„	85 „	
878	161 „	„	157 ± 4	

¹ For a still newer method, depending upon the damping of vibration of a quartz fibre, cf. F. Haber, *Zeitsch. Elektrochem.*, 20, 296, 1914.

² Smith and Menzies, *Journ. Amer. Chem. Soc.*, 32, 1434, 1910, have applied the formula to their measurements which extend over the range 250° to 435° C. The average deviation was only 0.050°. The actual expression used was: $\log p = 9.9073436 - 0.6519904 \log T - \frac{3276.628}{T}$.

The limitations of the formula will be apparent from the above comparative results. Its chief advantage is the wide range over which it is fairly accurate.

The empirical vapour-pressure formula of van der Waals may be written in the form—

$$\log \frac{p_c}{p} = f \left(\frac{T_c}{T} - 1 \right)$$

in which p is the vapour pressure corresponding to the temperature T , and f is regarded as a universal constant.

The following values of f were calculated from data obtained with carbon dioxide :—

Temperature, centigrade.	f .
+ 20	2·90
± 0	2·85
— 10	2·85
— 30	2·84
— 50	2·86
— 60	2·87
— 63·13	2·88

It will be observed that f is very nearly constant over this range of temperature. The following values of f were obtained in the case of a few typical substances :—

“NORMAL” SUBSTANCES (MOLECULES UNPOLYMERISED).

Substance.	f .	Substance.	f .
Hydrogen	2·10	Benzene	2·89
Nitrogen	2·27	Argon ¹	(2·18) 2·25
Oxygen	2·50	Krypton	(2·30) 2·39
Carbon dioxide . .	2·86	Xenon	(2·34) 2·38
Ether	3·01		

¹ More recently, Onnes (*Proc. Roy. Soc. Amsterdam*, **13**, 1019) finds that f for Argon increases from 2·415 (at $-140\cdot8^\circ$ C. and pressure 22·185 atmospheres) to 2·577 (at $+125\cdot49^\circ$ C. and 42·457 atmospheres), but there is no regularity in the variation.

"ABNORMAL" SUBSTANCES (MOLECULES POLYMERISED IN LIQUID STATE).

Substance.	<i>f</i> .
Water	3.26
Acetic acid	3.48
Methyl alcohol	3.75
Ethyl alcohol	3.91

The monatomic substances (Ar, Kr, Xe) appear to belong to a group by themselves. The value of *f* is not quite independent of the chemical nature of the substance under examination, this being especially so in the case of polymerised substances.

The pressure of saturated vapour depends only on the temperature, being independent of the volume of either phase as long as the volume of either phase is great compared with molecular dimensions.

Now the above vapour-pressure formula may be written in the "reduced" form thus—

$$\log p_r = f \left(1 - \frac{1}{T_r} \right)$$

and since the temperature fixes the pressure it follows from the principle of corresponding states that two bodies at corresponding temperatures, *i.e.* possessing the same value for *T_r*, must likewise be at corresponding pressures, *i.e.* possess the same value for *p_r*. Hence, even if *f* is not a universal constant and not even independent of temperature, it follows that it must have the same numerical value for substances in corresponding states.

MOLECULAR ASSOCIATION OR POLYMERISATION IN PURE LIQUIDS.

So far we have endeavoured to investigate the behaviour of liquids and gases from the purely physical standpoint, *i.e.* from the standpoint of distribution of molecules in space. The exceptions and discrepancies which arise, however, in this method of treatment seem only to have an explanation if we take into account the possibility of "chemical" effects such as

polymerisation or of dissociation of molecules themselves. The first point which arises is the question of the molecular weight of liquids actually *in the liquid state*. The usual methods of determining the molecular weight of a volatile substance are based upon determinations of vapour density, *e.g.* the methods of Dumas, Hoffmann or Victor Meyer (see Young's *Stoichiometry* for details). It is obvious, however, that the result one obtains by such means is the molecular weight of the body in the state of vapour. In water, for example, the result is 18, for ethyl alcohol 46, for benzene 78. Fortunately, there are one or two methods available which show the existence of polymerisation of molecules of certain liquids at least qualitatively. None of the methods is particularly sound, but the one most frequently employed is that known as the *Eötvös-Ramsay-Shields* method. It depends on a relationship first deduced by Eötvös in 1885 and applied as a practical method by Ramsay and Shields in 1893. Eötvös showed (*Annalen der Physik.*, 27, 448, 1885) from general considerations based upon the conception of corresponding states that the expression $\frac{d}{dt}\{\gamma(Mv)^{\frac{2}{3}}\}$, that is the temperature coefficient of the "molecular surface energy" (γ being surface tension, v the specific volume of the liquid, and M the molecular weight of the liquid as liquid), which could be represented by a curve of some kind obtained by plotting temperature against "molecular surface energy," $(Mv)^{\frac{2}{3}}$, should be the same type of curve for all substances. Having carried out some determinations with ether, he found experimentally that the curve was a straight line approximately, and hence the above expression $\frac{d}{dt}\{\gamma(Mv)^{\frac{2}{3}}\}$ was a constant. Eötvös wrote his relation in the form $\gamma(Mv)^{\frac{2}{3}} = k(T - T_0)$, where T_0 is a temperature not very different from the critical, k having the value 2.27. Note that Eötvös did not show theoretically that the expression should be a constant. What he did was to show that whatever shape the curve might be for one substance it would be the same for all others.

The experimental work of Ramsay and Shields (see

Young's *Stoichiometry*), however, while supporting Eötvös's generalisation in many cases, such as benzene, carbon disulphide, and series of esters, resulted in the discovery of marked discrepancies, notably in the cases of water, acetic and fatty acids in general, and the alcohols. These substances did not give the constant -2.1 (Ramsay and Shields' value of k), but gave a much smaller number. In working out these calculations the ordinary molecular weight, *i.e.* the molecular weight as given by *vapour density* determinations, was employed. Assuming the correctness of Eötvös's theoretical generalisation,¹ the most reasonable explanation of the anomalies which suggested itself was to consider the molecular weight of the "abnormal" substances as *differing* in the liquid and in the vapour states. As a matter of fact, in order to obtain the constant -2.1 it was necessary to ascribe a higher molecular weight to these substances in the liquid state than in the state of vapour. That is, a fraction of the molecules of these abnormal substances in the liquid state was regarded as associated or polymerised. The method of using the Eötvös formula for the calculation of M consists in writing it in the approximate form—

$$\frac{\gamma_0(Mv_0)^{\frac{2}{3}} - \gamma_1(Mv_1)^{\frac{2}{3}}}{t_0 - t_1} = -2.1$$

where γ_0 and v_0 refer to the temperature t_0 , and γ_1, v_1 to the temperature t_1 . Note that M is considered to be constant between t_0 and t_1 (an approximation). The expression for M is therefore—

$$M = \left\{ \frac{-2.1(t_0 - t_1)^{\frac{3}{2}}}{\gamma_0 v_0^{\frac{2}{3}} - \gamma_1 v_1^{\frac{2}{3}}} \right\}^{\frac{3}{2}}$$

For the experimental details of the determination of the surface tension, etc., reference must be made to the original paper (*Trans. Chem. Soc.*, **63**, 1089, 1893).

Besides observing that the constant obtained differed from -2.1 , in these associated liquids it was likewise found that its

¹ Eötvös's reasoning cannot be regarded as very rigid. See a paper by van der Waals, *Zeitsch. physik. Chem.*, **13**, 713, 1894.

value varied with the temperature, showing that the degree of dissociation varied with the temperature, tending towards unity, *i.e.* the normal molecular state, as the temperature rose. If we denote "degree of association" by n , *i.e.* the number of times the molecular weight is greater than its value in the state of vapour, we find the following :—

Water.		Acetic acid.		Methyl alcohol.		Ethyl alcohol.	
$t^{\circ}\text{C.}$	n	$t^{\circ}\text{C.}$	n	$t^{\circ}\text{C.}$	n	$t^{\circ}\text{C.}$	n
0	1.71	20	2.13	-90	2.65	-90	2.03
20	1.64	60	1.99	+20	2.32	+20	1.65
60	1.52	100	1.86	110	2.06	100	1.39
100	1.40	140	1.72	180	1.86	180	1.15
140	1.29	280	1.30	220	1.75	220	1.03

For a general discussion regarding the constitution of water, from which it seems fairly certain that ice consists mainly of trihydrol (H_2O)₃, together with a little dihydrol (H_2O)₂, and still less monhydrol, H_2O —liquid water at ordinary temperatures being mainly dihydrol with some trihydrol and some monhydrol, the latter increasing as temperature rises, the vapour being practically monhydrol—the reader is referred to the *Trans. Faraday Soc.*, 6, Part I., p. 71, 1910. It may be noted in passing that it is precisely those liquids which are themselves associated which, when acting as solvents, have the most marked property of causing dissociation, *i.e.* electrolytic dissociation, of many solutes such as acids, bases and salts.

It should be noted that the form of the Eötvös expression actually employed by Ramsay and Shields was somewhat different from that of the original, an empirical term d being introduced and the expression written thus—

$$\gamma(Mv)^{\frac{2}{3}} = k(\tau - d)$$

where τ is reckoned downwards from the critical temperature and d has usually the numerical value 6. The k in this expression, as used by Ramsay and Shields, has the value 2.12.

Recent investigation and discussion has, however, thrown

some doubt on the numerical values of the degree of polymerisation obtained by the above means, some authors considering that the estimates of Ramsay and Shields are too high, others that polymerisation is a much more general phenomenon and that possibly even normal liquids are not quite free from it. The whole problem is only very partially solved.

CHAPTER III

Chemical equilibrium in homogeneous systems (from the kinetic standpoint)—Gaseous systems—Deduction of the law of mass action—Reactions (in gaseous systems) involving no change in the total number of molecules—Reactions involving a change in the number of molecules—Effect of change of temperature and pressure upon the equilibrium constant.

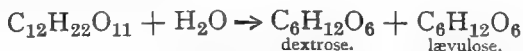
INTRODUCTORY

THE reason *why* a chemical reaction proceeds cannot be given in terms of the kinetic or molecular theory. From very early times the idea of affinity or chemical attraction between different kinds of matter had been generally recognised; the power of one body A to displace another B from a compound BC being attributed to the existence of a greater "affinity" between A and B than that between B and C. A good account of the historical evolution of the doctrine of affinity will be found in Mellor's *Chemical Statics and Dynamics*,¹ It is only relatively recently, however, that a more precise concept of affinity has been brought forward by van 't Hoff. This will be discussed in some detail in Part II. (Vol. II.) of this book. For the present we can only state that the reason why a reaction proceeds is directly connected with the energy of the system—not simply the kinetic energy of the particles, for indeed if the temperature of the system be kept constant throughout the reaction the kinetic energy of the particles will remain constant. We must defer consideration of the point until we are familiar with the principles of thermo-dynamics. It will be seen later that the chemical change is connected with a certain function of the system called the "entropy," the tendency of which is always to reach a maximum. It is an equivalent statement to say with regard to a reaction which proceeds at constant temperature and volume, that the change goes on until the "free-energy" of the system reaches a

¹ Sir William Ramsay's series of "Text-books of Physical Chemistry."

minimum. For the present, however, we simply accept the *fact* that a reaction does go until the final point is reached. When a reaction does not go completely, *i.e.* when the final point corresponds to a state of affairs in which the system contains some new products ("resultants") as well as some of the initial substances ("reactants"), this point is known as the "equilibrium point" of the reaction under the given conditions of temperature and pressure. It is our present business to find out what principles govern this equilibrium in the case of reactions occurring in homogeneous systems. A homogeneous system is one which consists of a single phase or portion of matter physically identical at all parts, *e.g.* a mixture of gases. A heterogeneous system, on the other hand, is one which consists of two or more homogeneous parts, *e.g.* liquid water in contact with water vapour.

The first important work carried out upon reactions in homogeneous systems was that of Wilhelmy (1850) (*Poggendorff's Annal.*, 81, 413, 499, 1850; *Ostwald's Klassiker*, No. 29), who measured the rate of the inversion of cane sugar $C_{12}H_{22}O_{11}$ in aqueous solution into dextrose and lævulose under the catalytic action of a small quantity of acid (hydrochloric or nitric). A "catalyst" (Berzelius) is a substance which has the property of hastening on a reaction without itself taking any definite part in the reaction. In the above case there is just as much acid remaining at the close of the reaction as there was at the beginning. We may, therefore, omit consideration of the catalyst as far as the stoichiometric equation representing the reaction



is concerned. Cane-sugar solution rotates a beam of polarised light to the right, that is cane sugar is dextro-rotatory, whereas the mixture of dextrose and lævulose is lævo-rotatory. Using a polarimeter Wilhelmy determined the rate of the reaction from the change in the angle of rotation at different time intervals. (By boiling the solution for some time the cane sugar is completely inverted, and the angular reading of the polarimeter given with this solution indicated the "final"

point in terms of the polarimeter readings.) Wilhelmy made the assumption that the rate at which the inversion took place, that is the quantity inverted in unit time, is proportional to the quantity of cane sugar still uninverted in the solution. This important assumption of Wilhelmy is the basis of the law of mass action. If the time be expressed by t and the quantity of sugar inverted after any given time be x , the velocity of inversion is $\frac{dx}{dt}$. This quantity $\frac{dx}{dt}$ is, according to Wilhelmy, proportional to the quantity of cane sugar remaining, which may be represented by $(a - x)$, where a is the original quantity of cane sugar when $t = 0$. Hence Wilhelmy's equation is—

$$\frac{dx}{dt} = k(a - x),$$

where k is a proportionality factor called the "velocity constant" of the reaction. On integration one obtains—

$$k = \frac{1}{t} \log_e \frac{a}{a - x} \quad \text{or} \quad k_1 = \frac{1}{t} \log_{10} \frac{a}{a - x}$$

where $k = 2.303k_1$.

Wilhelmy was the first to construct the differential equation quoted above for the calculation of a chemical reaction velocity.

Using nitric acid as the catalyst (at 15° C.) Wilhelmy succeeded in verifying the above equation experimentally, as will be seen from the figures in the following table :—

t (in minutes).	$a - x$ in polarimeter readings.	$\log \frac{a}{a - x}$	$k_1 = \frac{1}{t} \log_{10} \frac{a}{a - x}$
0	65.45	—	—
45	56.95	0.0605	0.00134
90	49.45	0.1217	0.00135
150	40.70	0.1981	0.00132
210	33.70	0.2880	0.00137
270	26.95	0.3851	0.00142

The (approximate) constancy in the values of k_1 is evidence for the validity of Wilhelmy's theory.

The idea of *reversibility* in chemical reactions which had been suggested by Berthollet was taken up at a later date by Malaguti (1853), (*Annales Chim. et Physique*, [3] 37, 198, 1853; 51, 328, 1857), who expressed the fundamental idea that chemical equilibrium—when it does occur—is due to the balance set up between two opposing reaction velocities in opposite senses. Malaguti as a matter of fact based his conclusion upon a heterogeneous not a homogeneous reaction, though the existence of equilibrium, as we shall see shortly, is more directly and conveniently demonstrated by some reactions occurring in homogeneous systems. Malaguti gave the first satisfactory explanation of a reversible reaction which had been observed by Marggraf in the eighteenth century, namely, the partial transformation of barium sulphate into barium carbonate and alkali sulphate by the addition of alkali carbonate, and the inverse reaction, namely, the production of barium sulphate by the addition of alkali sulphate to barium carbonate. Meanwhile, considerable advance had been made upon the subject of heterogeneous equilibrium in the case of solids in contact with gaseous decomposition products, notably in the case of calcium carbonate (solid), which on heating gives lime (solid) and carbonic acid gas, according to the equation—



Since calcium carbonate can be produced by bringing carbonic acid gas into contact with lime, an equilibrium state must be reached. Denoting the direction of a reaction by an arrow pointing either to left or right, it is usual to denote that such an equilibrium point is reached by rewriting the stoichiometric equation in the form $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$.

As early as 1837, Aimée (G. Aimée, reprint *Journal Physical Chem.*, 3, 364, 1899) stated that "when a body is decomposed by heat, it is not the pressure of any gas or vapour chosen at random which can stop its decomposition; it is the gas which arises from the decomposition which alone can act." This pressure, which is reached by the gaseous product (or products)

so that the system is in equilibrium at a given temperature, is known as the "dissociation pressure" of the solid substance. The further work of Groves,¹ St. Claire Deville,² and H. Debray,³ upon dissociation pressures and equilibrium points, yielded the following important conclusions:—

1. The dissociation pressure of a solid is constant at a given temperature.
2. The dissociation pressure increases with the temperature.
3. The dissociation pressure is independent of the amount of solids present (as long, of course, as there remains any of the original undecomposed solid).

The work which led, however, to the complete acceptance of the principle of equilibrium and a clear formulation of the law of mass action was that of Berthelot and Péan de St. Gilles (*Ann. Chim. Phys.* [3], 65, 385, 1862; 66, 5, 1862; 68, 225, 1863); of Harcourt and Esson (*Phil Trans.*, 156, 193, 1866; 157, 117, 1867; 186, 817, 1895); and especially from the theoretical standpoint the work of Guldberg and Waage (1864) (*Etudes sur les affinités chimiques*, Christiania, 1867; *Journ. prakt. Chem.*, [2] 19, 69, 1879; Ostwald's *Klassiker*, No. 104).

THE LAW OF MASS-ACTION (Guldberg and Waage).

The law of Mass-Action states that the rate at which a substance reacts is proportional to the *active mass* of the substance; and further that when chemical equilibrium is established this is due to opposing reaction velocities neutralising one another.

This law can be deduced from a kinetic molecular standpoint as well as from the standpoint of thermodynamics. We shall confine ourselves for the present to the kinetic method of deduction.

¹ Groves, *Phil. Trans.*, 137, 1, 1847.

² Deville, *Comptes Rendus*, 1857-1864, and *Leçons sur la dissociation*, Paris, 1866.

³ Debray, *Comptes Rendus*, 64, 603, 1867.

First of all, the term "active mass" requires some explanation. To obtain a simple idea of this term we must consider it as applying to reactions between gases in the first instance. (It will be shown later that it applies to reactions between substances dissolved in a solvent as well.) By "active mass" Guldberg and Waage understood what is usually termed the "molecular concentration" of the given substance, *i.e.* the number of molecules in a given volume of the gas or in the more frequently employed units, the number of gram-molecules per liter, or any term proportional to this, such as partial pressure.

Consider a simple type of reaction occurring in a homogeneous gaseous system at a given temperature. Let one molecule of a substance A react with one molecule of a substance B to produce one molecule of C plus one molecule of D, all these being gaseous substances. The ordinary or stoichiometric equation representing the reaction is—



If the reaction is one which reaches an equilibrium point at some stage—and all homogeneous gaseous reactions must do so, although in some cases the position of the equilibrium lies so far over to one side that the system consists *practically* of either reactants or resultants alone—the equilibrium state may be represented on the van 't Hoff notation by—



It is usual to denote the concentrations of these substances by the symbols C_A , C_B , C_C , C_D , or by simply enclosing the chemical symbol in a square bracket— $[A]$, $[B]$, $[C]$, $[D]$. These symbols denote concentration terms in general. Let us suppose the reaction has gone on until the equilibrium point is reached, at which point the concentration terms possess "equilibrium values," and may be denoted by C_{eA} , C_{eB} , C_{eC} , C_{eD} or $[A]_e$, $[B]_e$, $[C]_e$, $[D]_e$, (e is simply a suffix indicative of equilibrium).

Now the rate at which A and B are combining is taken to be proportional to the *product* of their concentrations, *i.e.* at the

equilibrium point the rate of combination is proportional to $C_{\epsilon A} \times C_{\epsilon B}$, or is *equal to* $k_1 C_{\epsilon A} \times C_{\epsilon B}$, where k_1 is a proportionality factor, namely, the velocity constant of the reaction from left to right. The employment of the product of the concentration terms and not any other function (such as their sum, for example) may be justified by considering a simple actual case.

“Suppose¹ we have a mixture in equal volumes of hydrogen and chlorine. A certain number of collisions in which an H_2 molecule strikes one Cl_2 molecule will occur in a second; and in some of these collisions combination will take place. Now let the concentration of the hydrogen be doubled, then twice as many H_2 molecules will collide with a Cl_2 molecule per second, and twice as much HCl will be formed. If the concentration of chlorine alone be doubled, the same effect will be produced, so that, if both concentrations are doubled, say, by compressing the gaseous mixture into half the volume, then four times as many collisions will occur in unit volume in unit time, and the velocity of the reaction, *i.e.* the amount of combination per second, will be quadrupled.” The velocity therefore with which the reaction takes place is proportional to the *product* of the concentration terms.

To return to the reaction $A + B \rightleftharpoons C + D$, it is evident that A and B combine (that is, disappear as such and appear as C + D) in equivalent amounts, namely, the disappearance of *one* molecule of A for one molecule of B. That is, A and B disappear at the same rate. Hence we can write in general—

$$\text{rate of disappearance of A and B} = k_1 C_A \times C_B$$

or at the equilibrium point—

$$\text{rate of disappearance of A and B} = k_1 C_{\epsilon A} \times C_{\epsilon B}$$

and this velocity or rate must be identical with the rate of *formation* of C and D. In exactly the same way we see that the rate of *disappearance* of C and D (to produce A and B) is given by the expression—

$$k_2 C_C \times C_D$$

¹ Leffeldt, *Textbook of Physical Chemistry*.

where k_2 is the proportionality factor or velocity constant of the reaction from right to left. At the equilibrium point we have—

$$\text{rate of disappearance of C and D} = k_2 C_{\epsilon C} \times C_{\epsilon D}$$

and this rate is identical with the rate of formation of A and B at the equilibrium point. Now at the equilibrium point it is clear that just as many molecules of A and B are disappearing per second as are formed per second. Hence at the equilibrium point we can equate the two velocity expressions given above. That is—

$$\begin{aligned} k_1 C_{\epsilon A} \times C_{\epsilon B} &= k_2 C_{\epsilon C} \times C_{\epsilon D} \\ \text{or} \quad \frac{C_{\epsilon C} \times C_{\epsilon D}}{C_{\epsilon A} \times C_{\epsilon B}} &= \frac{k_1}{k_2} = K \end{aligned}$$

where K is called the “equilibrium constant” of the reaction. We may equally well define the equilibrium state by employing the reciprocal of K —call it K_1 —in which—

$$K_1 = \frac{C_{\epsilon A} \times C_{\epsilon B}}{C_{\epsilon C} \times C_{\epsilon D}}$$

It will be observed that K (or K_1) is simply the ratio of two velocity constants, k_1 and k_2 , that is K is the ratio of the velocity constant of the reaction left to right, to the velocity constant of the reaction right to left. Since k_1 and k_2 always vary with the temperature and not necessarily to the same extent, it is evident that their ratio K , the equilibrium constant, may also vary with the temperature. In certain cases also which will be discussed later in connection with liquid systems, K varies with the pressure of the system. The problem of the shift of equilibrium with temperature and pressure can only be satisfactorily considered, however, from the thermodynamic standpoint. It is governed by the “principle of mobile equilibrium,” first introduced into chemistry by Le Chatelier and by Braun. It should be remembered therefore that when we speak of the equilibrium constant of a reaction, and assign a numerical value to it, it is necessary to state the temperature for which the numerical value holds.

To return to the equilibrium equation, it is sometimes convenient to express it in logarithmic form, viz.—

$$\log C_{\epsilon C} + \log C_{\epsilon D} - \log C_{\epsilon A} - \log C_{\epsilon B} = \log K$$

or, in general—

$$\Sigma \log C = K$$

where C denotes concentration in general, and $\Sigma \log C$ denotes the algebraic sum of the logs of all such concentration terms.

There are some points which still require further consideration. Thus we must be careful to distinguish between equilibrium concentration and any other concentration, say, the initial concentration. Let us consider the same reaction once more. Suppose we start with a gram-molecules of gas A, and b gram molecules of gas B in a vessel of volume v . Then the *initial* concentration of A is $\frac{a}{v}$, and the initial concentration

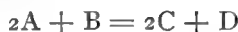
of B is $\frac{b}{v}$. These are *not* equilibrium concentrations (unless indeed we have previously added the requisite amount of C and D to the vessel so that the initial state is actually made identical with the equilibrium state). Suppose A and B only are present in the vessel. Reaction takes place, and let us suppose that equilibrium is reached when ϵ molecules of A have disappeared. Since the reaction is a very simple one, namely, *one* molecule of A reacting with *one* molecule of B to give *one* molecule each of C and D, it follows that when ϵ molecules of A disappear, the same number ϵ molecules of B will likewise disappear and ϵ molecules of both C and D will be produced. At the equilibrium point we have therefore $(a - \epsilon)$ molecules of A remaining, $(b - \epsilon)$ molecules of B, and ϵ molecules of C, and ϵ molecules of D. Since the volume v remains constant, the equilibrium concentration terms are—

$$\begin{array}{ll} \frac{a - \epsilon}{v} \text{ for A} & \frac{\epsilon}{v} \text{ for C} \\ \frac{b - \epsilon}{v} \text{ for B} & \frac{\epsilon}{v} \text{ for D} \end{array}$$

Hence the equilibrium constant K is given by—

$$K = \frac{\frac{\epsilon}{v} \times \frac{\epsilon}{v}}{\frac{a-\epsilon}{v} \times \frac{b-\epsilon}{v}} = \frac{\epsilon^2}{(a-\epsilon)(b-\epsilon)}$$

Let us now consider another type of reaction, in which more than one molecule of A—say two molecules—react with one molecule of a second substance B, giving rise, say, to two molecules of C and one molecule of D. The reaction is therefore represented by—



and the equilibrium point by—



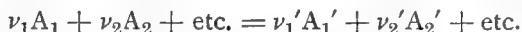
The rate of combination of the $2A$ and B depends on the kinetic basis upon the number of effective collisions between these substances in a given time. In the first reaction considered ($A + B \rightarrow C + D$) combination could occur when *one* molecule of A collided with *one* molecule of B . In the present case it is necessary that *two* molecules of A come into contact simultaneously with *one* molecule of B , so that the reaction from left to right may proceed. The rate of the reaction will therefore not simply depend upon the product of the concentration of A into the concentration of B , but will be governed by a somewhat more complicated function. The simplest way of considering such a reaction—though it is somewhat artificial—is to rewrite the equation as follows:—



and to regard the two A terms as separate entities as far as reactivity is concerned. The rate of reaction from left to right is therefore given by $k_1 C_A \times C_A \times C_B$ or $k_1 C_A^2 \times C_B$. Similarly the rate of reaction from right to left is $k_2 C_C^2 \times C_D$. Hence the equilibrium constant K is given by—

$$K = \frac{k_1}{k_2} = \frac{C_{\epsilon C}^2 \times C_{\epsilon D}}{C_{\epsilon A}^2 \times C_{\epsilon B}}$$

In an exactly similar manner we may deal with more complicated reactions still, the most general type of chemical reaction being represented by the stoichiometric equation—



which corresponds to the equilibrium relation—

$$K = \frac{C_{\epsilon A_1'}^{\nu_1'} \times C_{\epsilon A_2'}^{\nu_2'} \times \dots}{C_{\epsilon A_1}^{\nu_1} \times C_{\epsilon A_2}^{\nu_2} \times \dots}$$

or in the more convenient logarithmic form—

$$\sum \nu \log C = K$$

As already mentioned, one meets with the above mass action expression in the inverted form. It is purely a matter of convention.

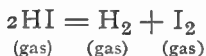
Another point requires a little consideration, namely, the use of the term “active *mass*.” It will have been observed that the essential quantity appearing in the foregoing treatment is concentration or mass per given volume. The use of the term “mass” in the expression “mass action” is therefore rather unfortunate. The expression should more correctly take the form “concentration action.” This will be clearly brought out when we come to study heterogeneous equilibrium such as the dissociation of calcium carbonate, in which it will be seen that the equilibrium point as measured by the concentration (or partial pressure) of the CO_2 is absolutely independent of the total *mass* of the solid carbonate—in fact, that the *active mass* of a solid is a *constant* whether the *actual* quantity present be great or small.

Having now considered the principle of mass action from the kinetic standpoint, we may pass on to consider some gaseous reactions in more detail.

HOMOGENEOUS GASEOUS REACTIONS.—FIRST-TYPE GAS REACTIONS,

i.e. reactions in which there is *no* change in the *total* number of molecules in the system.

Reactions of this type may be illustrated by the classic case of the dissociation of hydriodic acid according to the equation—



in which it will be seen that there are just as many molecules on the one side of the equation as on the other. The temperature is supposed to be sufficiently high so that the iodine is entirely in the state of vapour.

In purely gaseous reactions it has been found convenient to express the active mass not as a concentration term directly but in terms of the partial pressure of each component. The partial pressure of a gas in a gaseous mixture is proportional to the concentration of the gas. Thus in the above case if we write $p_{\epsilon\text{HI}}$ for the partial pressure of the unchanged HI when equilibrium is reached (p_{ϵ} = equilibrium partial pressure) at a given temperature, then $C_{\epsilon\text{HI}}$ is proportional to this quantity. That is $C_{\epsilon\text{HI}} = kp_{\epsilon\text{HI}}$. Similarly $C_{\epsilon\text{H}_2} = kp_{\epsilon\text{H}_2}$, and $C_{\epsilon\text{I}_2} = kp_{\epsilon\text{I}_2}$, so that the mass action expression is—

$$K = \frac{C_{\epsilon\text{H}_2} \times C_{\epsilon\text{I}_2}}{C_{\epsilon\text{HI}}^2} = \frac{kp_{\epsilon\text{H}_2} \times kp_{\epsilon\text{I}_2}}{k^2 p_{\epsilon\text{HI}}^2} = \frac{p_{\epsilon\text{H}_2} \times p_{\epsilon\text{I}_2}}{p_{\epsilon\text{HI}}^2}$$

This reaction has been very carefully studied by Lemoine (*Annales de Chim. et de Phys.*, [5] 12, 145, 1877), and at a later date and more thoroughly by Bodenstein and his pupils (*Zeitsch. phys. Chem.*, 13, 56, 1893; 22, 1, 1897; 29, 295, 1899). We shall therefore consider briefly some of Bodenstein's data upon this reaction, as these afford very satisfactory experimental confirmation of the validity of the law of mass action itself. Evidently the way to set about to verify such a law would be by carrying out a series of experiments in which the initial quantities of the reactants are altered, and after allowing equilibrium to be established in all the cases at the same temperature, one could calculate from the analyses of the

mixtures the respective values of the equilibrium constant and observe if agreement were obtained in the several cases. Another convenient way of demonstrating the same point is to carry out one or more experiments of the above kind, and so obtain a numerical value for the equilibrium constant, and then, by applying this value, calculate the quantity of some one of the components (say the HI), which should exist if the law is valid when equilibrium is reached in another experiment or series of experiments where new quantities of the reacting substances have been employed, and finally compare the found HI concentration with the calculated. The best method of demonstrating that a state of equilibrium really exists is to approach it from both sides. Thus, start with pure HI, allow a steady state to be reached at a certain temperature and calculate K . Then start with H_2 and I_2 at the same temperature, and again allow the reaction to proceed until no further change is noticeable, and again calculate K . If the two values of K agree, the principle is proved very conclusively.

The following illustrates one of the lines of investigation pursued by Bodenstein in the case of the hydriodic acid decomposition equilibrium. Let us express the degree of decomposition of the pure HI by x ; that is one gram-mole of HI is supposed to have reacted to such an extent that at equilibrium there are $(1 - x)$ moles of undecomposed HI, $\frac{x}{2}$ moles of H_2 and $\frac{x}{2}$ moles of iodine (vapour). [Note that *one* molecule of HI only gives rise to *one-half* a molecule of H_2 or I_2 .] If the volume of the vessel be v , and one such gram-molecule of HI had been originally introduced into it, then the equilibrium concentration terms are—

$$\begin{array}{ccc} \text{HI} & \text{H}_2 & \text{I}_2 \\ \frac{1-x}{v} & \frac{x}{2v} & \frac{x}{2v} \end{array}$$

$$\text{Hence } K = \frac{p_{\epsilon H_2} \times p_{\epsilon I_2}}{p_{\epsilon HI}^2} = \frac{C_{\epsilon H_2} \times C_{\epsilon I_2}}{C_{\epsilon HI}^2} = \frac{\frac{x^2}{4v^2}}{\frac{(1-x)^2}{v^2}} = \frac{x^2}{4(1-x)^2}$$

Let us now consider the reverse reaction, starting from a mixture of H_2 and I_2 , say a moles of iodine, and b moles of hydrogen in a volume v (which remains constant throughout the experiment), and let equilibrium be finally established when $2c$ moles of HI are formed. At the equilibrium we have therefore $(a - c)$ moles of I_2 ; $(b - c)$ moles of H_2 ; and $2c$ moles of HI . The equilibrium constant K is therefore given by the expression—

$$K = \frac{p_{\text{I}_2} \times p_{\text{H}_2}}{p_{\text{HI}}^2} = \frac{\frac{a-c}{v} \times \frac{b-c}{v}}{\frac{4c^2}{v^2}} = \frac{(a-c)(b-c)}{4c^2}$$

which solved¹ for c gives—

$$c = \frac{a+b}{2(1-4K)} - \sqrt{\frac{(a+b)^2}{4(1-4K)^2} - \frac{ab}{1-4K}}$$

The following data were obtained by Bodenstein:— a and b denote the number of cubic centimetres of gaseous H_2 and I_2 (reduced to 0°C . and 760 mm.) that were contained in the glass bulb of about 13 c.c. capacity. [a and b therefore represent *initial* concentrations; they do not represent equilibrium values.] It will be observed that in this reaction there is no necessity to determine the volume of the vessel with any accuracy at all as far as the equilibrium equation is concerned, for the v term cancels. It is not so, however, in other types of reactions, as we shall see later. $2c$ denotes the quantity of HI formed expressed in the same units. Bodenstein actually determined directly the quantities $(a - c)$, $(b - c)$, and c (or $2c$).

Temperature 357°C . (vapour of boiling mercury used as constant temperature bath).—The value of x was found experimentally to be 0.1946, the reaction considered being $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$. Hence K is calculated to be 0.01494. Using this value, $2c$ could be calculated for the series of

¹ In solving such equations there is no doubt about the sign before the root, as only *one* solution gives a physically possible result. In the above case, for example, a $+$ sign would yield values for c greater than $a + b$, which is, of course, impossible.

experiments in which H_2 and I_2 formed the initial mixture, *i.e.* $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$.

<i>a.</i>	<i>b.</i>	<i>zc</i> observed.	<i>zc</i> calculated.
2.59	6.63	4.98	5.02
5.71	6.22	9.55	9.60
10.40	6.41	11.88	11.68
26.22	6.41	12.54	12.34
23.81	6.21	12.17	11.98
22.29	6.51	12.71	12.68

Temperature 448°C . (sulphur vapour bath).—The value of x was found to be 0.2198. Hence K is calculated to be 0.01984. Note that at the higher temperature, x , and therefore K , has become larger, that is, the degree of decomposition of HI increases with the temperature. Using this value of K , zc is calculated as before.

<i>a.</i>	<i>b.</i>	<i>zc</i> observed.	<i>zc</i> calculated.
2.94	8.10	5.64	5.66
5.30	7.94	9.49	9.52
9.27	8.07	13.47	13.34
14.44	8.12	14.93	14.82
27.53	8.02	15.54	15.40
33.10	7.89	15.40	15.12

Bodenstein's results confirm the theory in a very satisfactory manner.

An important feature of the above reaction is that it involves no volume change, for although the nature of the molecules differs, the pressure produced only depends upon the number per unit volume, and this remains constant. In the other type of reaction, in which the number of molecules changes during the reaction, we can indeed keep the system at constant volume, but it will be found that the total pressure is not the same at the beginning and at the end. Examples of this type will be considered later. As further examples of the above type of reaction, mention may be made of the following:—

The formation and decomposition of hydrobromic acid and hydrochloric acid—



(Bodenstein and Geiger, *Zeitsch. phys. Chem.*, **49**, 70, 1904);



(Dolezalek, *Zeitsch. phys. Chem.*, **26**, 334, 1898).

Also the technically important reactions, namely, that dealing with the fixation of nitrogen from the air—



(Nernst, *Göttingen Nachrichten*, p. 261, 1904; Nernst, Jellinek, and Finckh, *Zeitsch. anorg. Chem.*, **45**, 116, 1905; **49**, 212, 1906; **49**, 229, 1906);

and the well-known water gas¹ equilibrium—



For details of these reactions the reader is referred to Haber's *Thermodynamics of Technical Gas Reactions*.

As already pointed out, a consequence of the absence of volume change in the above cases is that for all such reactions the numerical value of the equilibrium constant is the same, whether we express the active mass of the components either in concentration terms (gram molecules per liter) or in partial pressure terms (atmospheres). This can be seen at once by inspection of the equilibrium mass action equation, because the proportionality factor k connecting partial pressure with concentration occurs as often in the numerator as in the denominator, and therefore vanishes. On the other hand, suppose one considers a reaction in which there is a change in the total number of molecules as the reaction proceeds, thereby causing a change in volume (if the external pressure be kept constant), the numerical value of K will not be the same when expressed in concentration and partial pressure terms respectively. Thus, take the case of the decomposition of nitrogen peroxide—



¹ "Water gas" itself is produced by passing steam over heated carbon, thereby forming a mixture of CO_2 , CO , H_2 , and H_2O vapour. This mixture can be used as a gaseous fuel, since it gives out considerable heat when burnt with air.

In concentration terms—

$$K = \frac{C_{\epsilon \text{NO}_2}^2}{C_{\epsilon \text{N}_2\text{O}_4}}$$

Now $C_{\epsilon \text{NO}_2} = k p_{\epsilon \text{NO}_2}$ and $C_{\epsilon \text{N}_2\text{O}_4} = k p_{\epsilon \text{N}_2\text{O}_4}$

Therefore $K = \frac{k^2 p_{\epsilon \text{NO}_2}^2}{k p_{\epsilon \text{N}_2\text{O}_4}} = \frac{k p_{\epsilon \text{NO}_2}^2}{p_{\epsilon \text{N}_2\text{O}_4}}$

Writing $\frac{p_{\epsilon \text{NO}_2}^2}{p_{\epsilon \text{N}_2\text{O}_4}} = K_p$

we have $K = k K_p$

NOTE.—Instead of writing K with the significance attached to it above, another convention has been adopted by Haber (on the ground that it gives more convenient numerical values), in which the equation of the reaction is so written as not to include any molecular number greater than unity, though at the same time this necessarily means the introduction of fractional molecular numbers. Thus the decomposition of hydriodic acid would be represented by $\text{HI} = \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{I}_2$, and—

$$K_{\text{Haber}} = \frac{C_{\epsilon \text{H}_2}^{\frac{1}{2}} \times C_{\epsilon \text{I}_2}^{\frac{1}{2}}}{C_{\epsilon \text{HI}}}$$

which is evidently the square root of the previous K .

Let us return to the case of first-type gas reactions. One of the most important consequences of the characteristic absence of change in the total number of molecules is brought out when we consider what is *the effect of diluting* (i.e. *expanding*) or *concentrating* (i.e. *compressing*) such a system.

Suppose a certain mass of HI is brought into a vessel, and equilibrium is reached when the partial pressures are $p_{\epsilon \text{HI}}$, $p_{\epsilon \text{I}_2}$, $p_{\epsilon \text{H}_2}$ respectively, the total pressure being, say, 1 atmosphere, so that—

$$p_{\epsilon \text{HI}} + p_{\epsilon \text{H}_2} + p_{\epsilon \text{I}_2} = 1$$

the equilibrium constant K is—

$$\frac{p_{\epsilon \text{H}_2} \times p_{\epsilon \text{I}_2}}{p_{\epsilon \text{HI}}^2}$$

Now suppose we compress the system so that the *total* pressure is now two atmospheres. This is the same as doubling the

concentration, since the volume is only one-half its original size. Momentarily therefore in this case the partial pressures take on double their former values, and the expression becomes

$$\frac{2p_{\text{H}_2} \times 2p_{\text{I}_2}}{4p_{\text{HI}}^2}$$

which is identical with the former value. There is therefore no necessity for any "chemical" change to take place in the system in order that K may retain its former value. The state of things reached "momentarily" (*i.e.* at an imaginary period of time infinitely close to the moment when the alteration in the pressure of the system took place) is still an equilibrium state.

The fraction of HI dissociated or the degree of decomposition is therefore not altered in the slightest by the compression, nor would it have been altered, as may be easily seen, had we expanded the system, thereby decreasing all the partial pressures.

(In the second type of gas reaction, however, where there is a change in the number of molecules, it will be found that the "momentary state" is not an equilibrium state, but that some chemical change must take place in order to maintain K at its former numerical value.) In the hydriodic acid case no chemical change takes place on compression or rarefaction. The reasonableness of this conclusion may be demonstrated on the basis of the kinetic theory, as follows: ". . . before H_2 or I_2 can be produced, two molecules of HI must meet, and before the HI can be reformed a molecule of hydrogen must encounter a molecule of iodine vapour. The chances of each kind of encounter will be equally affected by a change in the concentration, so that the equilibrium established for one concentration will hold good at any other concentration. Although, therefore, the velocities [*i.e.* the $\frac{dx}{dt}$ terms, *not* the velocity constants] of the opposed reactions are altered by alteration in the concentration, they are altered to the same extent, and the position of equilibrium is unaffected" (Walker¹). This has been proved experimentally by Bodenstein. Thus, at 448°C .

¹ Professor James Walker's *Introduction to Physical Chemistry*.

Bodenstein found the following values for α , the degree of dissociation :—

Total pressure (in atmospheres)	0.5,	1.0,	1.5,	2.0
α	0.2019,	0.2143,	0.2225,	0.2306

According to the theory, α should remain constant, and this is seen to be approximately the case. The apparent rise in α is very probably due, as Bodenstein has suggested, to adsorption of the HI by the walls of the vessel.

EFFECT OF TEMPERATURE UPON THE EQUILIBRIUM CONSTANT.

It has already been mentioned that K varies with the temperature. This, as will be seen in the thermodynamic treatment of the problem, is essentially due to the fact that heat is evolved or absorbed by the reaction. It may also be regarded from the kinetic standpoint as due to the fact that the velocity constants k_1 and k_2 ($K = \frac{k_1}{k_2}$) vary with the temperature, and not necessarily to the same extent. To illustrate the extent of the variation of K in the case of the HI decomposition, a few of Bodenstein's values may be quoted. α again represents the degree of decomposition of the HI, so that $K = \frac{\alpha^2}{4(1 - \alpha)}$

$^{\circ}\text{C.}$	T abs.	α .	K.
280	553	0.17803	0.01172
360	633	0.19700	0.01504
460	733	0.22535	0.02115
520	793	0.24483	0.02625

EXPERIMENTAL METHODS OF MEASURING HOMOGENEOUS EQUILIBRIA IN GASES.—FIRST-TYPE GAS REACTIONS.

The methods may be divided into three classes:—(1) static methods, (2) dynamic methods, and (3) indirect methods.

(1) As an illustration of the static method, one may quote the following account of Bodenstein's measurements in connection with the HI, I₂, H₂ reaction.

A number of glass bulbs, each of about 15 c.c., are filled with HI gas at various pressures ($\frac{1}{2}$, 1, $1\frac{1}{2}$, and 2 atmospheres) at room temperature, and the bulbs sealed off. They were then heated in baths at known temperatures between 100°C . and 518°C . for given intervals of time. The bulbs were then removed, cooled as quickly¹ as possible, and opened under caustic potash, which dissolved the HI still remaining, as well as the iodine, the hydrogen remaining undissolved. Bodenstein then determined the volume of the bulbs, and hence the weight of HI originally contained in them. By measuring the quantity of hydrogen one could calculate the amount of I_2 , and likewise the amount of HI decomposed. In another series of experiments, the bulbs were filled with known amounts of H_2 and I_2 , reaction allowed to take place, the analyses being carried out in an analogous manner. The results of the two series of experiments—those in which the starting point is pure HI, and those in which the starting point is $\text{H}_2 + \text{I}_2$ —are shown in the figure (Fig. 21). The abscissæ represent the duration of the experiment, ordinates the fraction of HI present on opening and analysing. Note that the points marked on the curves do *not* represent equilibrium values (until the horizontal portion is reached), but simply the quantities of HI present at arbitrarily chosen time intervals. The curves show that in the early stages the reaction proceeds rapidly, but gradually slows down as the equilibrium point is approached. Notice that the two curves eventually coincide, that is, the same position of equilibrium is reached² from both sides. At 448°C . the equilibrium point corresponds to a 22 per cent. decomposition of the HI.

(2) The dynamic methods of measuring equilibrium are particularly suitable for reactions occurring at a high temperature. The methods consist in allowing the reacting gas mixture to

¹ This is known as chilling or freezing the equilibrium. It is assumed that the equilibrium ratios corresponding to the high temperature of the experiment have not had time to alter owing to the decrease in velocity as the temperature is quickly lowered.

² The effect of temperature on the rate at which equilibrium is reached is very marked. In this reaction at 440°C . the time is measurable in hours, at 350°C . in days, and at 250°C . months are required.

stream through a vessel kept at the required temperature, on passing out of which the gases are cooled as rapidly as possible. The chief difficulty is to get sufficiently rapid cooling. Since the gases are not, as a rule, in contact for a long time in the heated chamber, it has been found of the greatest advantage to employ some catalytic material in the heating vessel. If the catalyst is working properly, it has the property of hasten-

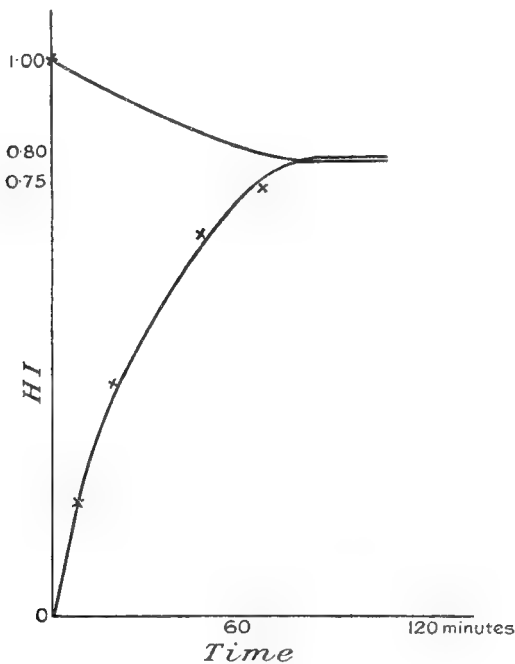


FIG. 21.

ing on a reaction without altering the equilibrium point, that is, the catalyst increases the velocity constants k_1 and k_2 of the direct and opposed reactions equally. The walls of the vessel have been shown by Bodenstein to act to a certain extent as a catalyst. Certain metals of the platinum group—especially platinum itself in a finely-divided form—have been found to be of great service as catalysts. In order to be certain that the composition of the emitted (and analysed) gas mixture

really corresponds to the equilibrium in the reaction chamber, one must vary certain of the conditions as much as possible, *e.g.* the arbitrarily chosen composition of the initial mixture, the velocity with which the gas mixture is caused to stream through the hot chamber, and the duration of the experiment. The temperature of the hot vessel is, of course, kept constant. The verification of equilibrium, having really been reached and determined, is best carried out by approaching the equilibrium point from both sides, as Bodenstein did in the case of the HI , H_2 , I_2 reaction.

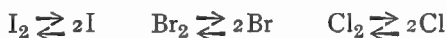
(3) The indirect method of determining equilibria—which, however, is less frequently resorted to than the direct—consists in measuring the reaction velocity constants k_1 and k_2 of the direct and opposed reactions, the equilibrium constant K being simply the ratio of these. These measurements have to be carried out at the earliest possible stage of the respective reaction. The reason of this will be clear when we come to discuss the chemical kinetics of opposed reactions.

SECOND-TYPE GAS REACTIONS,

i.e. those in which there is a change in the total number of molecules in the system during the reaction.

The simplest examples of this type are cases of gaseous dissociation. It is observed that while many gases and vapours give normal vapour densities—densities from which one can calculate molecular weights which are in agreement with the percentage composition of the substances as determined by analysis—many others give abnormal values, which can only be explained on the assumption that a certain number of the molecules have broken up into individuals of smaller molecular weight, thereby increasing the total number of individuals (*i.e.* increasing the volume if the pressure be kept the same), while the total *mass* of course remains the same. On raising the temperature of such a gas the density will naturally diminish, but it is found to diminish *more rapidly* than is to be expected on the kinetic theory when the rise in temperature only affects the distance of molecules apart

without affecting their number. As illustrations of second-type reactions, one may cite the decomposition of the halogens—

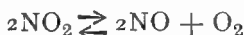


The dissociation of iodine vapour has been much studied, especially by Victor Meyer (*Ber.*, **13**, 394, 1880), and recently by Starck and Bodenstein (*Zeitsch. Electrochem.* **16**, 961, 1910). A similar reaction is the dissociation of nitrogen peroxide



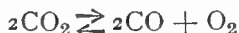
(E. and L. Natanson, *Wied. Ann.*, **24**, 454, 1885; **27**, 606, 1886).

At still higher temperatures the NO_2 molecules partially dissociate into NO and O_2 , according to the equilibrium equation—



(Richardson, *Journ. Chem. Soc.*, **51**, 397, 1887).

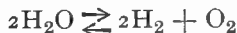
Further, carbon dioxide dissociates at high temperatures, giving rise to an equilibrium represented by the equation—



(Le Chatelier, *Zeitsch. phys. Chem.*, **2**, 782, 1888; Nernst and v. Wartenberg, *Zeitsch. phys. Chem.*, **56**, 534, 1906).

This reaction is of great importance in smelting furnace work.

Other examples are : The dissociation of water vapour—



(G. Preuner, *Zeitsch. phys. Chem.*, **42**, 50, 1903; Nernst and v. Wartenberg, *ibid.*, **56**, 534, 1906; Löwenstein, *ibid.*, **54**, 715, 1906; Langmuir, *Journ. Amer. Chem. Soc.*, **28**, 1357, 1906);

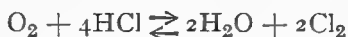
the dissociation of phosphorus pentachloride—



For the literature dealing with this reaction and the others mentioned, see Mellor's *Statics and Dynamics*.

In addition there are processes of great technical importance such as—

(a) The Deacon process of chlorine manufacture—



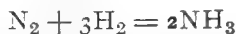
(Vogel v. Falckenstein, *Zeitsch. phys. Chem.*, **59**, 313, 1907; G. N. Lewis, *Journ. Amer. Chem. Soc.*, **28**, 380, 1906).

(b) The contact process of sulphuric acid manufacture, which depends essentially upon the reaction—



(Bodenstein and Pohl, *Zeitsch. Elektrochem.*, **11**, 373, 1905).

(c) The synthesis of ammonia—



(Haber and v. Oordt, *Zeitsch. anorgan. Chem.*, **43**, 111; **44**, 341, 1905; also Haber and Le Rossignol, *Ber.*, **40**, 2144, 1907).

As an illustration of the gaseous dissociation of an organic substance one may cite that of ammonium carbamate, which dissociates at 60° C., according to the equation—



For details of the technically important reactions referred to, the reader should consult Haber's *Thermodynamics of Technical Gas Reactions*.

Owing to the change in the number of molecules occurring in reactions such as the above, vapour density determinations have been frequently employed, since these show abnormal values from which the fraction dissociated and the dissociation constants can be obtained. Thus let us consider a gas which can undergo dissociation enclosed in a suitable vessel at constant temperature and suppose the density Δ measured. Suppose that we know the density δ of the gas if it were undissociated. This can be obtained by measuring the density at a lower temperature at which the gas is practically not dissociated at all. From this one can calculate by Gay-Lussac's Law what the density would be at the higher temperature if no dissociation took place. Suppose, however, that each gram-molecule dissociates at the higher temperature to a fraction α ,

then instead of one individual in a given volume we have $(1 + \alpha)$, supposing that the dissociation is of the simplest "binary" type, $A \rightarrow B + C$, one molecule giving rise to two smaller molecules or atoms. Now density is mass per unit volume, and the volume depends upon the number of individuals present, pressure being kept constant. Hence the density terms, *i.e.* the calculated and the observed, are inversely as the volumes containing the same mass. If Δ is the observed density at the higher temperature in question at which δ is the calculated or theoretical density, it follows that—

$$\frac{\Delta}{\delta} = \frac{1}{1 + \alpha} \quad \text{or} \quad \alpha = \frac{\delta - \Delta}{\Delta}$$

Now suppose one gram-molecule of the undissociated gas has been initially introduced into a vessel and the temperature raised, then when dissociation has taken place there are $(1 - \alpha)$ moles¹ of A, α moles of B, and α moles of C in a volume v , say, the corresponding concentration terms being $\frac{1 - \alpha}{v}$, $\frac{\alpha}{v}$, $\frac{\alpha}{v}$. The equilibrium mass-action equation is therefore—

$$\frac{C_{\epsilon C} \times C_{\epsilon B}}{C_{\epsilon A}} = \frac{\left(\frac{\alpha}{v}\right)^2}{\frac{1 - \alpha}{v}} = \frac{\alpha^2}{(1 - \alpha)v} = K_c$$

The "dissociation constant" K_c can therefore be calculated from α , which in turn is obtained from density determinations.

It is sometimes convenient to express the dissociation constant in terms of another easily measurable magnitude, namely, the total pressure P exerted by the system when equilibrium is reached. The expression also involves the δ and Δ terms.

Thus, taking the simple binary dissociation $A \rightarrow B + C$ as before, since the partial pressure of each molecular species depends upon the number of these particles in a given volume

¹ The term mole stands for gram-molecule.

(i.e. the concentration), it will be seen since p_B is identical with p_C —these being equal partial pressure terms—that—

$$\frac{p_A}{p_B} \text{ or } \frac{p_A}{p_C} = \frac{\frac{1-a}{v}}{\frac{a}{v}} = \frac{1-a}{a}$$

Hence
$$\frac{p_A}{p_A + p_B + p_C} = \frac{1-a}{1-a+2a} = \frac{1-a}{1+a}$$

But $p_A + p_B + p_C =$ sum of all the partial pressures
= total pressure P .

Hence
$$\frac{p_A}{P} = \frac{1-a}{1+a}$$

or
$$p_A = P \frac{1-a}{1+a}$$

This expresses the partial pressure of the undissociated molecules in terms of the total pressure of the system. It is clear from this expression that the degree of dissociation varies with the total pressure of the system. Writing α in terms of δ and Δ , one obtains—

$$p_A = P \left(\frac{2\Delta}{\delta} - 1 \right)$$

Similarly $p_B = p_C = p_A \left(\frac{a}{1-a} \right) = P \frac{a}{1+a} = P \left(1 - \frac{\Delta}{\delta} \right)$

The dissociation constant K_p —the constant obtained when partial pressure terms are employed instead of ordinary concentration terms (moles for liter), and which, as already pointed out, differs from K_c by a proportionality factor k —is given by the expression—

$$K_p = \frac{p_B \times p_C}{p_A} = \frac{P(\delta - \Delta)^2}{\delta(2\Delta - \delta)}$$

Expression for the dissociation constants K_c and K_p in terms of the total pressure P when dissociation is small.—Consider the reaction—



and suppose that a volume v contains altogether n moles of

water vapour of which a number nx are decomposed into hydrogen and oxygen. That is, the degree of dissociation is x . The concentration of the undissociated water vapour molecules is—

$$\frac{n - nx}{v} \quad \text{or} \quad \frac{n(1 - x)}{v}$$

Now from the above reaction equation it will be seen that two molecules of H_2O give on dissociating two molecules of H_2 + one molecule of O_2 . Hence nx molecules H_2O give rise to nx molecules of H_2 + $\frac{nx}{2}$ molecules of O_2 . Therefore the concentration of the hydrogen is $\frac{nx}{v}$, and that of the oxygen is $\frac{nx}{2v}$. Hence—

$$K_c = \frac{C_{\text{H}_2}^2 \times C_{\text{O}_2}}{C_{\text{H}_2\text{O}}^2} = \frac{\frac{n^2 x^2}{v^2} \times \frac{nx}{2v}}{\frac{n^2(1-x)^2}{v^2}} = \frac{nx^3}{2v(1-x)^2}$$

The total pressure exerted by the system in equilibrium is P . Suppose that the partial pressure of each constituent obeys the gas law, and let us further assume, as is the case in the dissociation of water vapour even up to very high temperatures, that the degree of dissociation x is very small. Then $Pv = nRT$, since there are approximately n molecules of water vapour present. Hence $v = \frac{nRT}{P}$, and therefore—

$$K_c = \frac{Px^3}{2RT(1-x)^2} \quad \text{or} \quad K_c = \frac{Px^3}{2RT}$$

neglecting x compared to unity.

$$\begin{aligned} \text{Further } K_p &= \frac{p_{\text{H}_2}^2 \times p_{\text{O}_2}}{p_{\text{H}_2\text{O}}^2} = \frac{(RT)^2 \cdot C_{\text{H}_2}^2 \times RTC_{\text{O}_2}}{(RT)^2 \cdot C_{\text{H}_2\text{O}}^2} \\ &= RT \times \frac{C_{\text{H}_2}^2 \times C_{\text{O}_2}}{C_{\text{H}_2\text{O}}^2} = RT \times K_c \\ &= RT \times \frac{Px^3}{2RT(1-x)^2} = \frac{Px^3}{2(1-x)^2} \end{aligned}$$

Suppose as a special case that the total pressure of the system is one atmosphere, and that x is small compared to unity, then—

$$K_p = \frac{x^3}{2}$$

The dissociation constant can thus be calculated very simply from the degree of dissociation when the latter is small.

EXAMPLES OF SECOND-TYPE GAS REACTIONS.

It will be convenient now to consider a few of the reactions already mentioned in order to see how far the law of mass action is confirmed by the results obtained. A simple case is the dissociation of iodine vapour according to the equation $I_2 \rightleftharpoons 2I$, recently investigated by Starck and Bodenstein (*Zeitsch. Electrochem.*, 16, 961, 1910), who have shown the existence of definite equilibrium points at various temperatures, and have measured the equilibrium constants very accurately. The apparatus employed consisted of a quartz bulb fitted with a quartz manometer working on the same principle as the Bourdon gauge. The temperature range over which the measurements were carried out varied from 800° C. to 1200° C. The following are some of the values obtained :—

$K_p = \frac{p_{eI}^2}{p_{eI_2}}$	Temperature (° C.).
0.0114	800
0.0474	900
0.165	1000
0.492	1100
1.23	1200

It will be observed that the dissociation into atomic iodine rapidly increases as the temperature is raised.¹ A similar

¹ Starck and Bodenstein also calculated by thermodynamics the heat effect involved in the reaction, and showed that the thermal effects were in agreement with Nernst's heat theorem (see Part II. (Vol. II.), Chap. XII.), which was not the case if one used V. Meyer's earlier data upon this reaction.

phenomenon is exhibited by first-type gas reactions, *e.g.* the decomposition of HI.

EFFECT OF PRESSURE ON THE DISSOCIATION IN SECOND-TYPE GAS REACTIONS.

At one and the same temperature the degree of dissociation, say, of iodine vapour, has been shown by experiment to be dependent upon the total pressure exerted by the vapour. The degree of dissociation increases the more dilute the system, *i.e.* the lower the pressure. It will be remembered that in first-type reactions (those involving no change in the total number of molecules) the effect of pressure upon the degree of dissociation was zero. This is the characteristic difference between first- and second-type reactions. The observed change of degree of dissociation in reactions involving a change in the total number of molecules is likewise satisfactory confirmation of the law of mass action, for such behaviour is predicted by the law. We may also anticipate the effect from the standpoint of the kinetic theory of gases. If we start with a given mass of gas occupying a certain volume under a given pressure, and increase the pressure, thereby reducing the volume, it seems reasonable to believe that this change does not affect the number of molecules of I_2 which dissociate per second, since each molecule dissociates, so to speak, of its own accord. The number of combinations per second of the separate iodine atoms will, however, be affected, for here each atom must meet a similar one in order to reform the original molecules of undissociated gas, and the number of times such combinations can take place will depend upon the collision frequency, this in turn upon the distance of the individuals apart, this again depending upon the volume occupied by the given mass of gas, and this finally depending upon the pressure. If therefore equilibrium is set up with a certain degree of dissociation under a given pressure, then on *increasing* the pressure (keeping the temperature constant, of course), the rate of combination of atoms will be favoured, the

ratio of dissociation of the molecules being left unchanged, with the result that the degree of dissociation will be *diminished*. The same conclusion is reached on the basis of the law of mass action. In the reaction $I_2 \rightleftharpoons 2I$ the dissociation constant K_c is given by the expression—

$$K_c = \frac{(\text{concentration of iodine atoms})^2}{\text{concentration of iodine molecules}}$$

Now if the pressure on the system be diminished, *i.e.* the volume increased, to such an extent that the concentration of the iodine atoms sinks to half its former value, the concentration of the iodine molecules would have simultaneously to sink to one-fourth their original value in order that K_c may remain constant. This means that the concentration of iodine molecules must decrease to a greater extent than the concentration of iodine atoms; in other words, some of them must cease to exist in the molecular form, *i.e.* the degree of dissociation is increased by diminishing the pressure.¹

This alteration in the degree of dissociation with pressure is characteristic of all reactions of the second type.

Data obtained in the case of Nitrogen Peroxide.—The application of the vapour density method to the dissociation of N_2O_4 into NO_2 has yielded the following results. Temperature 49.7°C .

¹ The effect of pressure in the above case is therefore to alter the degree of dissociation. In such gaseous reactions the equilibrium constant itself is not altered numerically, because concentration terms depend directly upon (*i.e.* may be written in terms of) pressure terms. Had the system been a liquid solution in which the pressure exerted upon the system bore no relation to the concentration terms of the substances reacting in the solution, then, as will be seen later (Part II. (Vol. II.), Chap. V.), in accordance with the principle of "mobile equilibrium" the equilibrium constant *itself* would alter numerically with alteration in externally applied pressure, provided the reaction is one which involves a volume change in the (liquid) system *as a whole*, no matter whether the reaction actually involves a "change in the number of molecules" or not, since volume changes in liquid systems are due to a variety of causes not effective in gaseous systems.

P.	Δ observed and referred to air as standard.	α	K_p .
0.0 mm.	—	1.000	—
26.80 „	1.663	0.930	106
93.75 „	1.788	0.789	112
182.69 „	1.894	0.690	124
261.37 „	1.963	0.630	130
497.75 „	2.144	0.493	121

The value of K_p if theory is correct should be constant. This is roughly the case; the variations being irregular.

The Deacon Process of Chlorine Manufacture.—The reaction involved in this process is represented by the equation



A careful experimental investigation has been carried out by Lunge and Marmier (*Zeitsch. angewandte Chem.*, 105, 1897). A mixture of hydrochloric acid gas and oxygen—the oxygen being sometimes replaced by air—was led over broken bricks which had been soaked in cupric chloride solution, then dried and heated to about 450°C . As a rule the gas mixture was originally dry, *i.e.* it contained no water vapour. The equilibrium was approached from one side only, *i.e.* the $\text{HCl} + \text{O}_2$ side, not from the chlorine-water-vapour side. The equilibrium equation in terms of partial pressures is—

$$\frac{p_{\text{H}_2\text{O}}^2 \times p_{\text{Cl}_2}^2}{p_{\text{O}_2} \times p_{\text{HCl}}^4} = K_p$$

or writing it as Haber does—

$$\frac{p_{\text{H}_2\text{O}}^{\frac{1}{2}} \times p_{\text{Cl}_2}^{\frac{1}{2}}}{p_{\text{O}_2}^{\frac{1}{4}} \times p_{\text{HCl}}^{\frac{1}{2}}} = K'_p \quad \text{where } K'_p = \sqrt[4]{K_p}$$

If a fraction x of each mole of HCl is decomposed when equilibrium is reached, this fraction will give rise to $\frac{x}{2}$ moles of chlorine, so that the ratio of the concentrations of these two constituents is, if v is the volume of the system—

$$\frac{\frac{x}{2v}}{\frac{1-x}{v}} = \frac{x}{2(1-x)} = \frac{p_{\epsilon\text{Cl}_2}}{p_{\epsilon\text{HCl}}}$$

Multiplying the equilibrium equation above and below by $p_{\epsilon\text{Cl}_2}^{\frac{1}{2}}$, one obtains—

$$\frac{p_{\epsilon\text{Cl}_2}}{p_{\epsilon\text{HCl}}} \cdot \frac{p_{\epsilon\text{H}_2\text{O}}^{\frac{1}{2}}}{p_{\epsilon\text{Cl}_2}^{\frac{1}{2}}} \cdot \frac{1}{p_{\epsilon\text{O}_2}^{\frac{1}{4}}} = K'_p$$

Now if we start with dry $\text{O}_2 + \text{HCl}$, we know from the stoichiometric equation $\text{O}_2 + 4\text{HCl} = 2\text{H}_2\text{O} + 2\text{Cl}_2$, that just as much H_2O vapour will be formed as chlorine vapour, so that the partial pressures of these two constituents will always be identical at any stage in the reaction, and therefore identical at the equilibrium point. Hence the term—

$$\frac{p_{\epsilon\text{H}_2\text{O}}^{\frac{1}{2}}}{p_{\epsilon\text{Cl}_2}^{\frac{1}{2}}} = 1$$

and, therefore—

$$K'_p = \frac{x}{2(1-x)} \cdot \frac{1}{p_{\epsilon\text{O}_2}^{\frac{1}{4}}}$$

This formula shows how relatively little the equilibrium point is influenced by the oxygen concentration or partial pressure, since it only occurs in the equation under a fourth root. Lunge and Marmier found that at the temperature at which they worked—in the region 400° – 500° C.—that the decomposition of HCl gas was large. When the initial mixture, for example, contained 8.5 per cent. HCl and 91.5 per cent. O_2 , the fraction x of the initial HCl decomposed was 0.83, *i.e.* 83 per cent. A difficulty met with in the experiments was the decomposition of the catalyst, the cupric chloride at the higher temperatures thereby interfering with the calculated chlorine content. The catalyst certainly volatilises in the region of 470° C., and traces go over at even lower temperatures. In experiments carried out above 500° C., it is evident that some of the

catalyst will be distilled into the cooler parts of the tube, and as the gas mixture passes over it in this region it will cause to some extent a change in the composition of the gas mixture (which has already reached equilibrium in the hottest portion) to another equilibrium state corresponding to the temperature of the cooler portion of the tube. Owing to this effect, it was found that the equilibrium constants, calculated from the results of experiments, carried out between 500° and 550° C., were not very different from those obtained at somewhat lower temperatures. This difficulty was got over later by Vogel von Falckenstein, who worked even up to 600° C., by using platinum chloride as catalyst at the higher temperature. The following table contains a few of the results of Lunge and Marmier at the temperature 430° C., starting with dry $\text{HCl} + \text{O}_2$.

Total pressure in mm	Initial mixture.		x .	$p_{\text{O}_2}^{\frac{1}{2}}$	$K'_p = \frac{x}{2(1-x)} \cdot \frac{1}{p_{\text{O}_2}^{\frac{1}{2}}}$
	%HCl.	%O ₂ .			
737	8.5	91.6	0.83	0.97	2.51
733	15.7	84.3	0.84	0.96	2.74
736.5	16.3	83.7	0.83	0.95	2.57
737	21.0	79.0	0.82	0.93	2.45
729	34.1	65.9	0.81	0.88	2.42
735	51.1	48.9	0.77	0.81	2.07
729	67.4	32.6	0.58	0.71	1.00*
725	83.1	16.9	0.39	0.55	0.58*

The average value for the equilibrium constant K'_p at this temperature is 2.4 approximately. It will be observed that some values—those marked with *—are considerably less than this. This is easily accounted for if the reaction had not yet reached the equilibrium state in the experimental vessel. The important point to observe is that the discrepancy manifests itself when the HCl percentage in the mixture becomes large. One would expect this to be the case, because, in order that a heterogeneous catalyst such as pumice saturated with CuCl_2 may hasten the reaction, the reactant molecules must come into contact with the surface of the catalyst, a

process which evidently depends on the actual extent of catalysing surface, and further, the greater the quantity of HCl to be decomposed, the longer the time required for every molecule to come into contact with the catalyst. In Marmier and Lunge's experiments with large quantities of HCl, the time presumably was not sufficient to allow the reaction to proceed to the equilibrium state, and hence the low values for the equilibrium constant. On using air instead of oxygen a similar discrepancy was observed when the HCl percentage was considerable, this being due to the dilution of the oxygen with the inert gas nitrogen, which also acted so as to slow down the rate at which equilibrium could be reached. To get the highest *percentage* of HCl decomposed, the conditions are small absolute quantity of HCl, and large absolute quantity of oxygen for a given quantity of catalyst at a given temperature. Thus in the first values given in the table the initial mixture contains only 8.5 per cent. HCl, and with it a large excess of O_2 , with the result that equilibrium is rapidly attained, the fraction of the HCl decomposed being large, namely, 0.83. Under the experimental conditions realised in the experiments referred to, equilibrium is evidently reached until the initial mixture contains 35 per cent. or more of HCl, provided pure oxygen is present to make up the remaining percentage composition of the mixture. If oxygen, however, is replaced by air, then even at 26 per cent. HCl in the initial mixture, the equilibrium is not yet reached at the conclusion of the experiment, the constant being somewhat low, namely, 2.14. Also in this latter case the fraction of the HCl decomposed is only 0.71, while it was as high as 0.81–0.82 when pure oxygen was used in place of air. The values of K'_p vary, of course, with the temperature. Thus Marmier and Lunge found that at 480° the average value for K'_p was 2.0. The results in this case were much more concordant than in that previously quoted. This is no doubt due to the higher temperature, since it is known that the velocity of reactions increases markedly with the temperature. In a homogeneous reaction, *i.e.* one occurring in the gaseous state or in solution, the general rule is that a rise of 10° causes the velocity constant to be doubled or even

trebled. The equilibrium point is therefore more rapidly reached at the higher temperature. It should be observed, however, that the numerical value of K'_p has diminished, with rise in temperature, and this means *ceteris paribus* that the quantity of chlorine formed from a given quantity of HCl is less than at lower temperatures. At the temperature 480° quite measurable quantities of chlorine were produced by decomposition of the catalyst. To obtain the optimum conditions for Cl_2 formation, one has therefore to take into account several factors such as prevention of decomposition of the catalyst, sufficient reaction velocity to reach equilibrium in reasonable time, and the temperature coefficient of the equilibrium constant itself. The results quoted will also serve to bring out how many factors go to determine the true realisation of the equilibrium point.

As already mentioned in the experiments referred to, the equilibrium point was only approached from one side. Vogel von Falckenstein (*Zeitsch. phys. Chem.*, **59**, 313, 1907; *Zeitsch. Elektrochem.*, **41**, 1906) has, however, carried out experiments in which it is approached from both sides, *i.e.* starting with a mixture of $\text{Cl}_2 + \text{H}_2\text{O}$ (vapour) as well as with a mixture of $\text{HCl} + \text{O}_2$. The following data were obtained, the "direct" process referring to those experiments in which the initial mixture consisted of $\text{HCl} + \text{O}_2$, the "reverse" process referring to the $\text{Cl}_2 + \text{H}_2\text{O}$ mixtures.

Temperature.	K'_p .		Mean K'_p .
	"Direct."	"Reverse."	
$^\circ\text{C.}$			
450	2.31	2.22	2.26
600	0.98	1.04	1.02
650	0.804	0.789	0.794

(The values for 600°C. are not based upon so many experimental determinations as those at the other temperatures.) The agreement between the values of K'_p obtained by the different processes is very satisfactory.

THE "CONTACT" PROCESS OF SULPHURIC ACID
MANUFACTURE.

The essential reaction involved here may be represented by—



The equilibrium constant is—

$$\frac{p_{\epsilon\text{SO}_3}^2}{p_{\epsilon\text{SO}_2}^2 \times p_{\epsilon\text{O}_2}} = K_p$$

or

$$\frac{p_{\epsilon\text{SO}_3}}{p_{\epsilon\text{SO}_2} \times p_{\epsilon\text{O}_2}^{\frac{1}{2}}} = K'_p$$

The "contact" process derives its name from the fact that the $\text{SO}_2 + \text{O}_2$ gas mixture is passed over a solid catalyst—finely divided platinum—in contact with which the above reaction proceeds. A fairly full account of the literature will be found in Haber's *Thermodynamics of Technical Gas Reactions*. It is only necessary here to refer to some work of Bodenstein as illustrative of how such a reaction is investigated from the technical physico-chemical standpoint. Bodenstein's method consists in passing a mixture of $\text{SO}_2 + \text{air}$ over hot platinised asbestos, contained in two quartz vessels. Combination takes place in the first vessel, thereby liberating a large amount of heat, which alters the temperature of the catalyst, and consequently tends to set up an equilibrium corresponding to this higher (unknown) temperature. The mixture when equilibrium is almost reached is transferred to the second vessel, and since the amount of transformation yet to be undergone is small, the heat effect is likewise small, so that the true equilibrium point corresponding to the temperature of the enclosure is realised. Temperature changes have a most marked effect upon this reaction. Some data will be given in the section dealing with the variation of K with the temperature. The advantage of using platinum in some form lies in the accelerating influence it exerts on the reaction, so that at temperatures below 500° equilibrium is reached sufficiently quickly to

allow of the employment of rapid currents of gas, which is, of course, a highly important technical point where time is a factor which must always be considered. Without a catalyst the reaction is extremely slow below 500° , and if we raised the temperature sufficiently so as to allow of fairly rapid realisation of equilibrium, it would be found that the equilibrium point now corresponds to considerable dissociation of SO_3 , *i.e.* only a relatively small amount of $\text{SO}_2 + \text{O}_2$ combines at high temperatures. It will be seen at once therefore how much the technical success of such a process depends upon the use of a good catalyst, which causes the reaction to go at a satisfactory rate under temperature conditions which are favourable to high percentage yield of the desired product. The above process, for example, was at first of no technical importance—compared to the older chamber process—owing to the want of a suitable catalyst, and later, even after platinum was in use for the purpose, the process again lost favour owing to some alteration of the platinum on continued use, which rendered it ineffective as a catalyst. This has been traced to the presence of impurities in the SO_2 , which must be carefully eliminated before the gas mixture comes into contact with the catalyst, as otherwise a process known as “poisoning the catalyst” takes place. As a matter of fact, practically nothing is known as to what this poisoning really is—probably because we are still much in the dark regarding the mechanism of the catalysing effect itself. Recently it has been stated in connection with the SO_3 production that a certain rise in temperature will get over the difficulty of the poisoning without causing the formation of SO_3 to diminish too much.

VARIATION OF THE EQUILIBRIUM CONSTANT WITH TEMPERATURE.

Just as in the first-type gas reactions, so in those of the second-type, the numerical values of K_c and K_p or K'_p vary with the temperature. Some instances have already been given in connection with *the Deacon process*. A few more for

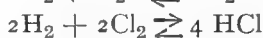
the same reaction are here added for the sake of completeness.

Temperature.	K'_p found.	Experimenter.	K'_p calculated by Haber.
°C.			
352	4'02	G. N. Lewis	4'57
386	3'02	"	3'40
419	2'35	"	2'62
430	2'50	Lunge and Marmier	2'42
450	2'26	v. Falckenstein	2'10
480	2'0	Lunge and Marmier	1'73
600	1'02	v. Falckenstein	0'90
650	0'794	"	0'728

The values of K'_p found were obtained by dynamic methods. As an indirect method one may call attention to the column of values headed K'_p calculated, which were obtained on a thermodynamical basis from certain energy relations applied to the separate reactions—



and



which on subtraction yield the Deacon equation. The ideas involved in this calculation cannot be understood until the reader has familiarised himself with the principles of Thermodynamics (Part II. (Vol. II.), Chaps. I. and II.). The temperature effect, as already pointed out, is of great technical significance. It is clear from the above data that the position of equilibrium becomes more favourable for the preparation of chlorine, the lower the temperature. In this process, therefore, the highest percentage transformation of HCl into chlorine would theoretically be obtained by working at as low a temperature as possible. A lower limit is, however, set to the temperature by the fact that with decrease in temperature the velocity of formation likewise diminishes. Technical work has shown that the best results are obtained if the reaction is carried out in the region of 400° C.

The data available in connection with the *contact process* of sulphuric acid manufacture are interesting as showing an

exceedingly marked temperature influence. Haber (*l.c.*) gives the following table of K'_p values based on Bodenstein's data, the constant K'_p standing as before for—

$$\frac{p_{\text{SO}_3}}{p_{\text{SO}_2} \times p_{\text{O}_2}^{\frac{1}{2}}}$$

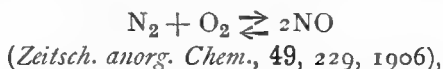
Temperature.	K'_p
°C.	
528	31·3
579	13·8
627	5·54
680	3·24
727	1·86
789	0·956
832	0·627
897	0·358

At 450° Haber calculated from Knietsch's observations that K'_p was as much as 187·67, whilst it is only 0·358 at 897°. A large constant indicates large formation of SO_3 , hence the lower the temperature the better the yield. It should be remembered that equilibrium values are always the maximum values for a given temperature which can possibly be obtained in any process, and hence the importance of studying these technical problems from the physico-chemical standpoint by means of which it is possible to say quantitatively—not empirically—when the limit of yield has been reached under given conditions. The condition of low temperature in the above case must, however, not be carried too far, for here again the question of time comes in, as it is of little benefit to know that a large yield may be obtained if expenditure of time be too great for its realisation.

EXPERIMENTAL METHODS OF DETERMINING EQUILIBRIA IN SECOND-TYPE GAS REACTIONS.

The methods may be divided as before into (1) static, (2) dynamic, (3) indirect (velocity constant measurements). We have already dealt with several instances of the first two

methods. One point requires to be emphasised. Among static methods we find frequent use made of density determinations. This method is quite characteristic of second-type gas reactions, for it is only possible by this method to tell anything about the course of a reaction if the reaction itself involves a change in the total number of molecules and therefore gives rise to "abnormal" density values. To first-type gas reactions the density method is quite inapplicable. Dynamic methods on the whole are more generally in use, especially as many gas reactions are carried out at high temperatures, for which such methods are well suited. The experiments quoted in the case of the Deacon process and the contact sulphuric acid process are examples of dynamic methods. The indirect method of determination of equilibrium points by means of the velocity constants of the "direct" and "reverse" reaction is quite analogous to that employed in first-type gas reactions. As an example, the reader is referred to Nernst and Jellinek's determination of the equilibrium constant of the reaction—



which is of great technical importance in connection with the problem of the fixation of atmospheric nitrogen.

THE EFFECT OF ADDING VARIOUS SUBSTANCES TO SYSTEMS ALREADY IN EQUILIBRIUM.

Two important cases arise in this connection :—

First, what is the effect of adding an indifferent gas (*i.e.* one which does not react chemically) to a gas system already in equilibrium, (*a*) the addition of the indifferent gas being made at constant volume, (*b*) the addition causing an increase in volume at constant pressure?

Secondly, what is the effect of adding one of the components of the reaction to a system already in equilibrium, (*a*) the volume being kept constant, (*b*) the volume being allowed to increase?

As regards the first question, both types of gas reaction may be considered simultaneously. On adding an indifferent gas to a gaseous system representing, say, a dissociation equilibrium ($\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ or $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$) and keeping *the volume constant*, it is evident that the total pressure must increase. *Experience has shown that the percentage dissociation or decomposition is not altered thereby.* This is an agreement with what one would expect on the basis of Dalton's Law, for by this law the presence of a foreign inert gas does not influence the partial pressures exerted by the reacting components. This holds equally well whether the reaction itself involves a change in the total number of molecules or not. This behaviour must not be confused with the effect of increased pressure on second-type gas reactions, which we have already discussed, and in which we found that increasing the pressure or decreasing the volume caused a certain amount of recombination to take place. In the case of *compression* simply, the point to be noticed is that the increase in pressure was carried out in such a way that the partial pressure of *each* component was increased, while in the case of the addition of the inert gas the *total* pressure is increased (at constant volume) while each partial pressure remains unaltered. Now we come to the second part of the first question, viz., what happens if we add an indifferent gas to a gas system in equilibrium in such a way that the volume of the system increases while the *total* pressure remains the same? Here we have evidently diluted the system. Now it has already been seen that in first-type gas reactions the equilibrium is unaffected by volume (*e.g.* HI , H_2 , I_2), and therefore there is no change in the fraction dissociated in such a case, though, of course, the absolute values of the partial pressures have fallen since the same mass of each component is now distributed throughout a larger volume. In the case of second-type reactions the result is different. The increase of volume at constant pressure causes, as we have seen, an increase in the dissociation products. By the addition of the indifferent gas we have—just as in first-type reactions—decreased the partial pressure of each reacting component, and in second-type reactions the

fraction dissociated depends on the total pressure exerted by the components, which is now less than before although the total pressure of the system remains constant. Hence the effect of dilution is to cause dissociation of second-type reactions to *increase*.

We may summarise the above effects as follows :—

Addition of inert gas.	{	<p>If volume is kept constant : no chemical change in both first- and second-type reactions.</p> <p>If volume increases : no chemical change in first-type reactions. Increase in dissociation (the dissociation <i>constant</i> remaining the same, of course) in the second-type reactions.¹</p>
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EFFECT OF ADDING ONE OF THE REACTING CONSTITUENTS, THE SYSTEM BEING KEPT AT CONSTANT VOLUME.

DIVISION A.—FIRST-TYPE REACTIONS.

These must be further subdivided into : (1) Reactions in which *one* kind of chemical substance gives rise to one other kind ; (2) one kind of substance yields two or more different kinds ; (3) two or more kinds give rise to two or more different kinds still. It will be convenient to work with concrete examples :—

Subdivision (1).—No examples are known. Isomeric changes would belong to this group, but none are known in gases.² Let us take the hypothetical case $1A \rightleftharpoons 1B$ for which the equilibrium constant is $\frac{C_{\epsilon B}}{C_{\epsilon A}}$, what is the effect of adding

¹ Dissociation is a particular kind of a second-type reaction. In general one may say that diluting a second-type reaction—the total pressure being kept constant—causes the reaction to go toward the side of the equation which contains the greater number of molecules, *i.e.* in the reaction, $1A + 2B \rightleftharpoons 3C + 4D$, the effect of dilution in the above manner will be to cause an increase in C and D.

² Perhaps the active modification of nitrogen, recently discovered by Strutt on passing electric sparks through nitrogen, may belong to this group, but nothing is known regarding this point.

some B, keeping the volume constant? The pressure obviously will be increased. A simple way of finding out what is likely to happen in all these cases where some constituent is added, is to imagine the state which is reached "momentarily" on adding the gas in question. That is, we imagine the gas added so quickly (yet without any heat effects) that the rest of the system remains as it was during this moment even if it should ultimately alter. The method is perhaps a little artificial, but it allows one to predict what will happen assuming the applicability of the law of mass action. If experience in all cases is in agreement with the prediction, it obviously affords very conclusive proof of the validity of the law.

Let us consider now what happens on increasing the concentration of B by adding it to the system at constant volume. "Momentarily" we have A at concentration $C_{\epsilon A}$ and

B at concentration C'_B , and the expression $\frac{C'_B}{C_{\epsilon A}}$ is therefore

greater than before, and hence if we are to have a constant at all it is clear that a chemical change must take place in the system whereby the concentration of B decreases and A increases, *i.e.* the reaction goes thus $B \rightarrow A$.

Similarly, had we added excess of A, the reaction would have gone in the opposite direction. The effect therefore of adding excess of either of the components in this case is to cause part of this excess to be used up in the production of some of the other component. The net effect therefore is that the *concentration* of *both* components is increased. In spite of this, however, the *fraction decomposed* of A, say, is not altered from the former state, because the ratio of the concentrations of A and B must remain constant, and this can be written in the form—

$$\frac{\frac{x}{v}}{1 - \frac{x}{v}}$$

(where x is the fraction of one mole of A which disappears to give rise to B), an expression which is obviously independent

of the dilution v (and therefore of the concentration which is the reciprocal of v) since this quantity v cancels out, leaving

$\frac{x}{1-x}$ constant and therefore x constant.

Subdivision (2).—An example is the familiar reaction $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$. What is the effect of adding excess of H_2 to this system when in equilibrium, keeping the volume constant? According to the law of mass action—

$$\frac{p_{\epsilon\text{H}_2} \times p_{\epsilon\text{I}_2}}{p_{\epsilon\text{HI}}^2}$$

is constant (at a given temperature). “Momentarily” we shall have the pressure of the H_2 increased, say, to p'_{H_2} , and the expression—

$$\frac{p'_{\text{H}_2} \times p_{\epsilon\text{I}_2}}{p_{\epsilon\text{HI}}^2}$$

would now be too large, so that in order that the equilibrium constant may retain its original value, part of the H_2 and I_2 must unite to give some HI , *i.e.* the decomposition of HI is thrown back. Evidently just as much HI will thus be formed as corresponds to I_2 disappearing in the process. Analogous results would have been obtained had we added excess I_2 vapour instead of H_2 . We may therefore generalise by saying that the degree of decomposition of HI is diminished by the addition at constant volume of either of the products of decomposition. By preferentially adding only one of the products of decomposition we bring about a state of things which might be called “an asymmetrically decomposed system,” because the products are not present in equivalent quantities. Such an asymmetric state never occurs as a result of spontaneous action, but can be brought about in the manner above described. When we speak of “the degree of decomposition” in such a case as the above, it is not quite the same as the ordinary decomposition into equivalent amounts of H_2 and I_2 . By adding H_2 we have decreased I_2 and accordingly increased the HI . Hence the ratio $\frac{\text{I}_2}{\text{HI}}$ has decreased, and if we add a

large amount of H_2 we can make the I_2 almost vanish. It is *this* degree of dissociation which decreases, *i.e.* dissociation with respect to the constituent which has *not* been artificially increased. This does not contradict the conclusion to which we came earlier, namely, that the degree of dissociation of any first-type reaction is independent of the volume or concentration of the system, for then we were only thinking of symmetrical decomposition into equivalent amounts of H_2 and I_2 . This can be seen at once if we imagine the effect which will be produced if we add H_2 and I_2 simultaneously in equivalent amounts. In order to keep the equilibrium constant the same, H_2 and I_2 will combine to a certain extent, the uncombined portions necessarily remaining in equivalent quantities. The result of such a proceeding will be to increase the *concentration* of all the constituents, namely, the HI , H_2 , and I_2 , but the *degree* of decomposition will be absolutely unaltered, for evidently we could have arrived at the same state not by adding H_2 and I_2 in equivalent quantities, but by simply compressing the system. Clearly the same reasoning applies if we add HI to the original system. In this case the expression—

$$\frac{p_{H_2} \times p_{I_2}}{p^2_{HI}}$$

would momentarily be too small, and hence some of the HI will decompose, but this it can only do symmetrically into equivalent H_2 and I_2 , so that, although each concentration or partial pressure term is increased, the fraction decomposed is unaltered. If, however, we make the composition of the system asymmetric by preferential addition of one of the products of decomposition as already stated, the degree of dissociation with respect to the other product is decreased. In this type of reaction the student must be careful not to make the statement that the addition of any constituent will alter the degree of decomposition, for, of course, HI itself is a constituent, and we have seen that the addition of this does not alter the degree of decomposition. The whole matter may be simply put thus: if symmetrical change is caused in

the system at constant volume (by addition of HI), the degree of decomposition remains unchanged; if the system becomes assymmetric by the addition of one product of decomposition, the degree of decomposition with respect to the other product is decreased. The difference between subdivisions (1) and (2) is now clear, because under no circumstances can we make the reaction of subdivision (1) assymmetric. The student must also bear in mind that we are discussing first-type reactions only.

Subdivision (3).—This includes reactions such as that represented by the equation—



or more generally—



where

$$n_1 + n_2 = n_3 + n_4$$

and the substances A, B, C, and D are all different. Each substance can be added in turn, so that concentration asymmetry can be introduced into the system from either side of the equation. This distinguishes such reactions from that of subdivision (2), in which asymmetry could only be brought about from one side (*i.e.* in the hydriodic acid decomposition by addition of either H_2 or I_2). As an illustration we may consider the water gas reaction—



for which the equilibrium constant K_c is—

$$\frac{C_{eH_2O} \times C_{eCO}}{C_{eCO_2} \times C_{eH_2}}$$

If one adds at constant volume *either* water vapour or carbon monoxide, formation of some $CO_2 + H_2$ results. Similarly, addition of either carbon dioxide or hydrogen causes the production of some $H_2O + CO$. We can no longer speak of degree of decomposition in such a case, since all the substances are different, and a single substance does not of itself produce any other substance. In so far as investigation has gone in gaseous reactions, no exception has been met with as regards the law of mass action,

DIVISION B.—SECOND-TYPE GAS REACTIONS.

We have now to consider second-type gas reactions as regards the effect of adding components to a system already in equilibrium, the system being kept as before *at constant volume*. It is not necessary to make any subdivisions here. It will be remembered that these reactions are characterised by the fact that the degree of dissociation—when the reaction happens to be simply a dissociation such as $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$ —alters with the dilution of the system. The following statement holds good:—If to a second-type reaction system in equilibrium we add at constant volume *any* one of the constituents the degree of dissociation is thereby altered. This happens whether the dissociation is made symmetrical or not. Consider the simple type of reaction represented by the dissociation of molecular iodine into atomic iodine, according to the equation $\text{I}_2 \rightleftharpoons 2\text{I}$. The equilibrium constant—

$$K_c = \frac{C_{\epsilon\text{I}}^2}{C_{\epsilon\text{I}_2}}$$

If we could imagine iodine *atoms* added, the pressure rises since the volume is kept constant, and consequently we get formation of I_2 molecules, but, for reasons given when discussing the effect of external pressure in such a case, not only is the absolute concentration of each constituent increased, but at the same time the degree of dissociation of the iodine molecules is decreased. The degree of dissociation would be simply—

$$\frac{\text{concentration of I}}{\text{concentration of I}_2}$$

and it is clear that this cannot be constant, since it is the expression—

$$\frac{(\text{concentration of iodine atoms})^2}{\text{concentration of iodine molecules}}$$

which remains constant. The degree of dissociation, as well as the absolute concentration terms of each constituent is likewise altered by addition of molecular iodine—this being the only practical addition we can make,

Further, take the case in which two different products are formed by dissociation, *e.g.* the dissociation of phosphorus pentachloride, $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$. The temperature is supposed to be such that all the constituents are gaseous. The equilibrium constant is—

$$K_c = \frac{C_{\text{PCl}_3} \times C_{\text{Cl}_2}}{C_{\text{PCl}_5}} \quad \text{or} \quad K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}}$$

Suppose some chlorine is added, the “momentary” state is evidently not one of equilibrium, the above expression being now greater than before. Partial combination of PCl_3 and Cl_2 occurs, giving rise to some PCl_5 . The system is also at a higher pressure now than it was previous to the addition, and hence the degree of dissociation of the PCl_5 is less. The addition of one of the products of dissociation therefore throws back the degree of dissociation, just as in first-type reactions¹ at constant volume. Also if some PCl_5 be added, the above expression is momentarily too small, and hence some of the PCl_5 added dissociates. The total pressure (due to the sum of the partial pressures) has increased, and therefore the degree of dissociation of PCl_5 is once more decreased. An exactly similar effect would of course have been produced by adding $\text{PCl}_3 + \text{Cl}_2$ in equivalent quantities. In first-type reactions, however (HI , H_2 , I_2), the degree of decomposition of the HI is not affected by addition of HI , although of course the absolute concentration values of each constituent is increased if the volume be kept constant. For second-type reactions (“dissociations”) it is therefore quite correct to say that addition of *any* constituent at constant volume will decrease the degree of dissociation; for first-type reactions it is only by adding *certain* constituents, so as to set up a state of “asymmetric decomposition” that the degree of decomposition is thrown back (with respect to the constituent not artificially increased).

Further, let us consider the Deacon process—



¹ The system being thereby made “asymmetric,”

which gives a constant—

$$K_p = \frac{p_{\epsilon\text{Cl}_2}^2 \times p_{\epsilon\text{H}_2\text{O}}^2}{p_{\epsilon\text{O}_2} \times p_{\epsilon\text{HCl}}^4}$$

This might be considered as a second-type reaction analogue of the water-gas reaction $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}$. The behaviour of the Deacon reaction resembles the water-gas reaction in that the addition of any *one* of the constituents causes a general increase in the concentration of all the constituents, in order to keep K_p constant, the volume, having been kept unchanged. There is the following marked difference, however. If one adds in the Deacon reaction some $\text{Cl}_2 + \text{H}_2\text{O}$ in the correct stoichiometric quantities required by the reaction equation (one mole of each), some $\text{HCl} + \text{O}_2$ will be produced, *i.e.* the absolute values of the concentrations are increased, and since the addition has been made at constant volume, the pressure has risen, but the *ratios* of the numerator terms to the denominator terms must not remain the same as before, for if this were the case it is obvious that raising *some* of them to different powers as they appear in the equilibrium equation would not when thus raised yield the same value for K . In the water-gas reaction, however, the addition of $\text{H}_2\text{O} + \text{CO}$ in stoichiometric quantities leaves the equation in such a state that the ratios of the numerator terms to those of the denominator, *i.e.*—

$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{CO}_2}} \quad \text{or} \quad \frac{p_{\text{CO}}}{p_{\text{H}_2}} \quad \text{or} \quad \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$$

are just the same as they have been previous to the addition. The absolute values of the concentration terms are, of course, increased.

We may now pass on to the final part of the problem, namely :—

WHAT EFFECTS ARE PRODUCED IN FIRST- AND SECOND-TYPE GAS REACTIONS BY THE ADDITION OF DECOMPOSITION OR DISSOCIATION PRODUCTS, THE SYSTEM BEING KEPT AT CONSTANT PRESSURE?

The volume of the system evidently increases to a greater or less extent under these conditions. The case is scarcely so important as the preceding, but it is, nevertheless, of interest to see what behaviour the law of mass action predicts. We shall not trouble to treat the two types of reaction separately. Instead, we shall simply consider one or two special cases.

(i) The reaction involves the dissociation of one kind of molecule into two new kinds, *e.g.* the dissociation of phosphorus pentachloride, $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$. The condition for equilibrium is that—

$$\frac{\frac{x}{v} \times \frac{x}{v}}{\frac{1-x}{v}} = \text{constant, } K$$

where x is the mass of chlorine or phosphorus trichloride (in moles) present in the volume v (liters), and $(1 - x)$ is the mass of phosphorus pentachloride. x is therefore the degree of dissociation or fraction of one mole of PCl_5 dissociated. Now suppose nv liters of Cl_2 or PCl_3 are added at the same partial pressure at which these substances exist in the mixture. Consider the "momentary" state. The volume increases to $(n + 1)v$ liters while the total pressure of the system remains the same as before, since the Cl_2 or PCl_3 has been added at its original partial pressure. The original partial pressure of Cl_2 or PCl_3 corresponded to a concentration of x moles in v liters. By adding nv liters under the same conditions we have added nx moles of chlorine (say), so that the total mass of chlorine is now $(n + 1)x$ moles, and this is "momentarily" distributed throughout a volume $(n + 1)v$, so that its concentration is $\frac{(n + 1)x}{(n + 1)v}$.

During the "momentary" state therefore we have the following concentration relations—

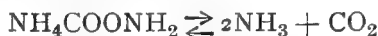
$$\frac{\frac{x}{(n+1)v} \cdot \frac{(n+1)x}{(n+1)v}}{\frac{1-x}{(n+1)v}}$$

which is evidently identical with the former expression—

$$\frac{\frac{x}{v} \times \frac{x}{v}}{\frac{1-x}{v}}$$

In other words, the "momentary" state in this case turns out to be an equilibrium state. Hence the addition of either Cl_2 or PCl_3 at the same partial pressure as that already existing in the equilibrium mixture, so that the system increases in volume while the total pressure remains constant, has no influence on the degree of dissociation of the PCl_5 . This conclusion should be compared with that when Cl_2 or PCl_3 is added, the system being kept at constant volume, in which case the degree of dissociation is thrown back.

(ii) The reaction involves a dissociation wherein *one* molecule of a substance gives rise to *three* molecules, *two* of which are identical, *e.g.* the dissociation of ammonium carbamate into ammonia and carbon dioxide—



The equilibrium constant is given by—

$$K = \frac{\left(\frac{x}{v}\right)^2 \times \frac{x}{v}}{\frac{1-x}{v}}$$

where x is the fraction dissociated of one mole of $\text{NH}_4\text{COONH}_2$. First of all, suppose we add m liters of CO_2 at the same partial pressure as that already possessed by the CO_2 in the

equilibrium mixture. The total pressure is constant, the volume increasing to $(n+1)v$ liters. The total mass of CO_2 is $(n+1)x$ moles and the above expression becomes—

$$\frac{\left\{ \frac{x}{(n+1)v} \right\}^2 \times \frac{(n+1)x}{(n+1)v}}{\frac{1-x}{(n+1)v}}, \text{ which is equal to } \frac{\frac{x^2}{(n+1)v^2} \times \frac{x}{v}}{\frac{1-x}{v}}$$

And this is no longer equal to the original mass action expression. The numerator has decreased, and in order that the constant K may remain as such, the numerator terms, that is, the dissociation products, must increase. *Hence the effect of adding the CO_2 under the above conditions is to cause the carbamate to dissociate further.*

Now consider what happens if NH_3 be added instead of CO_2 . Suppose nv liters of NH_3 added at the partial pressure already obtaining in the equilibrium mixture. The mass of NH_3 is now $(n+1)x$ in the volume $(n+1)v$, and hence the mass action expression is at the momentary state—

$$\frac{\left\{ \frac{(n+1)x}{(n+1)v} \right\}^2 \times \frac{x}{(n+1)v}}{\frac{1-x}{(n+1)v}} = \frac{\left(\frac{x}{v} \right)^2 \times \frac{x}{v}}{\frac{1-x}{v}}$$

which is identical with the original value. Hence the degree of dissociation of the carbamate is in this instance unchanged. If $\text{NH}_3 + \text{CO}_2$ were added, each at the correct partial pressure, it will be seen on setting up the equation that the degree of dissociation of the carbamate will be thrown back.

(iii) Finally, consider the reaction $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$. The condition for equilibrium is that—

$$\frac{\frac{x}{v} \times \frac{x}{v}}{\frac{1-x}{v}} \quad \text{or} \quad \frac{x^2}{(1-x)^2}$$

shall be constant.

If nv liters of hydrogen be added at the correct partial pressure the momentary state will be represented by—

$$\frac{\frac{(n+1)x}{(n+1)v} \times \frac{x}{(n+1)v}}{\left\{ \frac{1-x}{(n+1)v} \right\}^2} \quad \text{or} \quad \frac{(n+1)x^2}{(1-x)^2}$$

The numerator is now too large, and in order that the equilibrium constant may retain its original value the decomposition of the HI must be thrown back.

The behaviour of systems which undergo volume increase at constant total pressure by the addition of one or more of the reacting constituents differs from case to case, but it can in general be foretold by applying the law of mass action.

It may be pointed out that writing the volume increase as the sum of the original mixture and added gas only holds in certain cases when equilibrium is finally reached. If we take those cases in which no change is produced in the degree of dissociation by the addition, then the equilibrium volume is actually the "momentary" volume. In other cases, however, in which the addition causes the dissociation to alter, it will be found that finally, *i.e.* at the equilibrium state, the volume is not simply the sum of the original plus added gas, but has some other value in order to keep the total pressure constant. If the degree of dissociation is thrown back there will be an actual disappearance of molecules, and the final volume will be less than the momentary volume in order that the total pressure may be constant. The opposite effect occurs when the dissociation has been increased by the addition. The device of the "momentary" state is of great use, however, in telling us qualitatively at any rate what will happen.

CHAPTER IV

Chemical equilibrium in homogeneous systems (*continued*)—Liquid mixtures
—Solutions—Properties of solutions.

THE systems to be considered may be divided into (1) liquid mixtures, and (2) solutions. The terms are not employed very rigidly, the term solution being not infrequently applied to include liquid mixtures as well. The distinction, such as it is, refers to the relative quantity in which the various constituents of the system coexist. The term "liquid mixture" applies strictly to a homogeneous liquid system in which no single constituent is present in very large excess compared to the other constituents. The separate constituents are at the same time liquids. A (liquid) solution, on the other hand, is a liquid system in which one liquid—called the solvent—is present in large excess. The constituents dissolved in the solvent are known as "solutes." Solutions may be produced by dissolving solids, liquids, or gases in a given solvent. The latter functions as the medium in which the reaction takes place and may in certain cases take a definite part in the reaction. In other cases—and these are the most frequently occurring—no definite *rôle* can be assigned to it, *i.e.* it does not appear in the stoichiometric equation representing the reaction, but apparently functions as an inert medium. The properties of solutions and the types of equilibria which are found vary much according to the chemical nature of the solvent, for this determines to a certain extent the nature of the individuals produced by dissolving a given solute.

It has already been shown that the law of mass action is a satisfactory guide as far as gaseous reactions are concerned. Reaction there takes place between molecules, between atoms, and between molecules and atoms. We did not have to deal

with electrical effects.¹ In liquid systems, however, besides reactions between molecules similar to gaseous molecules, we sometimes find instances of reactions between electrically charged particles called "*ions*," which are atoms or radicals carrying electricity proportionate to their valency. Ions occur most frequently in aqueous solutions of substances known as "*electrolytes*," notably inorganic acids, salts, and some bases, *e.g.* solutions of caustic potash, hydrochloric acid, sodium chloride, etc. Ions also occur, though to a much less extent, in solutions of similar substances in acetone, methyl alcohol, ethyl alcohol, or in a few other organic solvents. Solutions in which liquids such as hydrocarbons (aliphatic and aromatic) act as solvents do not contain ions, or at most only a very few. Ions may be of two kinds, according to the sign of the electrical charge carried, namely, positive ions or cations and negative ions or anions. Solutions are, however, in all cases electrically neutral, as the anions and cations are always present in equivalent numbers.

In addition to reactions between ions, we also find reactions occurring between (uncharged) molecules and ions. As a matter of fact, when ions are produced some molecules are likewise present though in certain cases to a very small extent. Reactions in liquids may therefore be more complicated in nature than those which occur in gases. The law of mass action has, however, been applied to equilibrium in liquid systems with considerable success. In such cases we take as a measure of the active mass of a constituent its concentration reckoned in moles per liter of solution, whether the constituent is electrically charged or not.

For the purpose of systematising our study we may classify reactions into (1) reactions in liquid mixtures, and (2) reactions in solutions. Reactions in solution are those which, as already mentioned, take place in a suitable liquid medium—the solvent—which is present in large excess, but which does not

¹ In the case of a gas which has been ionised by electrical discharge, or by the rays of radio-active substances mentioned in Chapter I., the rate of combination of electrified particles to yield a neutral gas appears to follow the mass action principle.

take part *apparently* in the reaction. Though the equilibrium relations can be satisfactorily studied in many cases without taking the solvent into account except as an inert diluent, it would be rash to suppose that it actually plays no part, since the nature of the solvent frequently determines the nature of the dissolved particles of solute. In certain solvents the solute may give rise to ions, that is to say, the solute may suffer "electrolytic dissociation"; in others, even the same solute will be quite unable to ionise. In other cases still, a definite stoichiometric part is played by the solvent as in the hydrolysis of salts in aqueous solutions. For convenience we shall consider equilibria involving ions in the next chapter, under the head of the "electrolytic dissociation theory," since this forms by far the most important branch of reactions in liquid systems.

I. LIQUID MIXTURES.

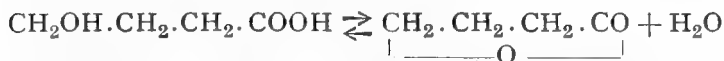
Our present purpose is to see how far the law of mass action has been established for reactions between uncharged liquid molecules when these are not suspended in a solvent—inert or otherwise—but are simply spatially distributed in the manner peculiar to the liquid state.

As an example, we may consider the *change of ammonium thiocyanate into thiourea*, according to the equation—



At ordinary temperatures both these substances are solids and each may be kept for an indefinite time without alteration. This is due to the fact that reactions in the solid state are always very slow. The change, however, has been studied in the liquid state by working at a higher temperature, $152^\circ\text{--}153^\circ\text{C.}$, at which the system is in a state of fusion. Experiments have been carried out by J. Waddell (*Journ. Phys. Chem.*, 2, 523, 1898), beginning with each substance in turn. The same equilibrium point corresponding to the above temperature was reached from both sides, the equilibrium mixture being 21.2 per cent. thiocyanate and 78.8 per cent. thiourea. A little doubt exists regarding the numerical accuracy of the

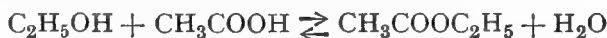
above numbers owing to the fact that the materials were not absolutely pure.¹ The results show quite definitely, however, that an equilibrium point is actually reached. The difficulty of applying the law of mass action, however, in such a case lies in what one means by "concentration" and whether concentration (moles per liter) is a true measure of the active mass. A similar type of reaction is met with in the conversion of γ -oxybutyric acid into γ -butyrolactone.²



investigated by P. Henry (*Zeitsch. physik. Chem.*, **10**, 98, 1892). Starting with 18.23 moles of the acid, it was found that equilibrium was reached when 13.28 moles had been transformed. There were therefore 4.95 moles of acid left. If the volume of the system is v litres, the concentration of acid at the equilibrium point is $\frac{4.95}{v}$, that of lactone or water being $\frac{13.28}{v}$, and

the equilibrium constant $K = \frac{(13.28)^2}{4.95^2}$. The experiments being carried out for a different purpose, Henry did not investigate the constant further. Fairly good velocity constants were obtained, however, and this is evidence that mass action is effective in bringing about the state of equilibrium.

The most thoroughly investigated case of equilibrium in a liquid mixture is that furnished by the *action of ethyl alcohol upon acetic acid*. According to the equation—



This reaction was studied by M. Berthelot and Péan de St. Gilles (*Ann. Chim. Phys.*, **65**, **66**, 1862; **68**, 1863). The reaction goes slowly at ordinary temperatures, several days being required to reach the equilibrium point. It may, however, be reached in a few hours by sealing up the mixture of alcohol and acid in a glass tube and heating to about 100° C. The stage reached after any interval of time may be determined in this case by titrating the acetic acid

¹ See Mellor, *Statics and Dynamics*, p. 86.

² *Ibid.*, p. 82.

present. This method is only allowable if the reaction is a very slow one, no measurable change in the state of the system, *i.e.* no fresh acid being produced, during the time taken for titration. In reactions which go more rapidly this method would be quite inapplicable; in such cases we must have recourse to the measurement of some physical property which can be made without altering the relative concentrations of any of the reacting substances. Berthelot and St. Gilles established the fact that the same equilibrium point is reached whether we start with alcohol and acid or with ethyl acetate and water. Employing one mole of each substance to start with, on allowing the respective pairs to react the same equilibrium point was reached in both cases, namely: $\frac{1}{3}$ mole acetic acid, $\frac{1}{3}$ mole ethyl alcohol, $\frac{2}{3}$ mole ethyl acetate, $\frac{2}{3}$ mole water. After the lapse of several years these ratios were found to be absolutely unchanged.

Let us now calculate the equilibrium constant for the above case. Suppose the volume of the system is v liters.

Equilibrium concentrations are:—

Acetic acid.	Ethyl alcohol.	Ethyl acetate.	Water.
$\frac{1}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$
$\frac{1}{v}$	$\frac{1}{v}$	$\frac{2}{v}$	$\frac{2}{v}$

$$\begin{aligned} \text{The equilibrium constant } K &= \frac{C_{\epsilon \text{ ester}} \times C_{\epsilon \text{H}_2\text{O}}}{C_{\epsilon \text{ acetic}} \times C_{\epsilon \text{ alcohol}}} \\ &= \frac{(\frac{2}{3})^2}{(\frac{1}{3})^2} = 4 \end{aligned}$$

It will be observed that the above reaction is one which does not involve a change in the number of molecules. The v term, therefore, vanishes. If the system were gaseous, change of pressure would have no effect upon the numerical value of the *degree* of decomposition of the acid or alcohol.

Even in a reaction such as the above, however, where there is no change in the *number* of reacting molecules there may be slight volume change owing to the different cohesion attractions or repulsions possessed by the molecules of the different species produced in the liquid state. If there is absolutely no change in volume as the reaction proceeds, change in external pressure

can have no effect upon the value of the constant K . If on the other hand, there is a slight volume change of the system as a whole, produced as a result of the reaction, then the value of K will be (slightly) affected by alteration in the external pressure. Usually the effect is so very small that it may be neglected; theoretically, however, it is present, being analogous to the change of K with temperature, both effects being instances of the principle of "mobile equilibrium."

Returning to the equilibrium equation, it will be seen that it may be put in a somewhat more general form by supposing that the initial mixture consists of 1 mole of acetic acid, m moles ethyl alcohol, and that equilibrium is reached when x moles of ethyl acetate (or water) are formed. Then

$$K = \frac{x^2}{(1-x)(m-x)}$$

Employing the numerical value of K obtained from the experiment already quoted, we can calculate x for any other case and compare it with the value given by experiment. The following table is due to van 't Hoff (*Ber.*, 10, 669, 1877), the values being based upon Berthelot and St. Gilles' data.

Initial quantity of acetic acid.	Initial quantity of alcohol.	x calculated.	x found
1 mole	0.05 mole	0.049 mole	0.05 mole
"	0.18 "	0.171 "	0.171 "
"	0.33 "	0.311 "	0.293 "
"	0.50 "	0.423 "	0.414 "
"	1.00 "	0.667 "	0.667 ¹ "
"	2.00 "	0.845 "	0.858 "
"	8.00 "	0.945 "	0.966 "

The agreement between calculated and found values is extremely good. We are, therefore, justified in regarding the law of mass action as applicable to reactions in liquid mixtures. The same reaction has recently been reinvestigated by Jones and Lapworth (*Trans. C. S.*, 99, 1427, 1911), using hydrochloric

¹ This result was used for the calculation of K in the first instance, hence the agreement in the last two columns is necessarily exact.

acid as the catalysing agent to hasten the course of the reaction. Their results are very important from the standpoint of the mechanism of such catalysis, for they consider they have succeeded in showing that part of the HCl unites with part of the H_2O , thereby virtually removing part of the latter from active participation in the Berthelot reaction, with the result that calculations made of the equilibrium constant on the basis that all the water present is *active* lead to a series of different values for K —"apparent" values denoted by the symbol ψ —according to the amount of HCl in the system. Berthelot and St. Gilles did not employ a catalyst. The following account of Jones and Lapworth's experiments is given in their own words.

The equilibrium constant $K = \frac{[\text{H}_2\text{O}][\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5]}{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{CO}_2\text{H}]}$ is known to be approximately 4 for the homogeneous liquid system over a very wide range of temperature, its value being but slightly affected by the addition of small quantities of catalysts, by alterations in the relative amounts of the constituents, or by the use of various indifferent solvent media.

Whilst the activity of hydrogen chloride in alcohol is greatly diminished by small amounts of water, it is but imperceptibly affected by acetic acid or by ethyl acetate; hence, if the variations in the availability of hydrogen chloride are, in fact, due to combination of the latter with water, then hydrogen chloride, when passed into an equilibrium mixture of water, ethyl acetate, alcohol, and acetic acid, should unite almost exclusively with the water when the latter is there in considerable quantity. The experience of Berthelot and Péan de St. Gilles with indifferent solvents would lead to the conclusion that the value of K , corrected for the quantities of the four constituents removed by the hydrogen chloride and rendered inert, would still remain nearly constant. The present paper, *i.e.* that of Lapworth and Jones, describes measurements of this kind, which show that as the ratio of the amount of water existing in equilibrium to the amount of hydrogen chloride falls, the value of ψ (the apparent value of K calculated on the assumption that the water in the system is entirely in the free

state) rises from 4 to 8 at least, indicating clearly that some of the water present combines with the hydrogen chloride. Further, assuming that this apparent variation in the "constant" is, as suggested, due to hydrate formation, it may be calculated that, roughly, two molecules of water associate with each molecule of hydrogen chloride present, although the existence of higher hydrates in a partly dissociated condition is not excluded.

The procedure in each of the experiments was as follows. Ordinary test-tubes were subjected to the action of a current of steam, dried, constricted near the open end, and weighed. By means of narrow thistle-funnels passed through the constriction in the test-tube, quantities of ethyl acetate and hydrochloric acid were introduced. The tube was weighed after each such addition, and then sealed off at the constriction, when it was immersed in a bath, kept at $25^{\circ} \pm 0.20^{\circ}$, and frequently shaken. The mixture became homogeneous after about one to two hours when 7.268N-hydrochloric acid was used, and the tubes were broken and their contents analysed after forty to fifty-eight hours; in experiments Nos. 1 and 4, however, thirty-five days elapsed before they were removed from the bath. When 0.1185N-hydrochloric acid was employed, complete admixture did not occur until after nearly three weeks, and in such cases the tubes were not removed before thirty-six days. The dried tubes were finally broken in excess of carefully neutralised sodium acetate solution, which was then diluted to a litre, portions of 100 c.c. being taken and titrated against standard baryta solution, with phenolphthalein as indicator. The amount of hydrogen chloride which remained was checked by means of standard silver nitrate. The results of the experiments are summarised in the table.

In line A are given the numbers of the experiments.

"	"	B	"	"	weights of ethyl acetate taken.
"	"	C	"	"	weights of 7.268N-hydrochloric acid.
"	"	D	"	"	weights of 0.1185N-hydrochloric acid.
"	"	E	"	"	amounts of hydrogen chloride taken in gram-molecules.

In line F are given the amounts of hydrogen chloride found at the end of the experiment.

„ „ G „ „ total titre (acetic acid plus hydrogen chloride) in c.c. of normal acid.

In lines H, K, and L are given the total apparent number of gram-molecules of acetic acid (and alcohol), of water, and of ester, respectively, found at equilibrium.

In line R are given the ratios $[\text{H}_2\text{O}(\text{total})]/[\text{HCl}]$ in each case.

In line S are given the values of ψ .

$$\psi = \frac{[\text{H}_2\text{O}(\text{total})][\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5]}{[\text{CH}_3\text{CO}_2\text{H}][\text{C}_2\text{H}_5\text{OH}]}$$

The apparent value, $\psi = 4.35$, experiment No. 14, corresponds with the formation of 0.6761 gram-molecule of ethyl acetate and of water from 1 gram-molecule of acetic acid and of ethyl acetate. Berthelot and Péan de St. Gilles (*loc. cit.*) found that, at 9°, 1 gram-molecule of ethyl alcohol and of acetic acid combined to form 0.665 gram-molecule of ethyl acetate and of water, in the absence of hydrogen chloride ($[\text{H}_2\text{O}]/[\text{HCl}] = \text{infinity}$).

A	1.	2.	3.	4.	5.	6.	7.	8.
B	12.3121	11.7921	11.3334	10.4887	11.1817	8.0458	7.0384	10.1819
C	2.0154	1.9992	3.9524	3.9337	4.6554	6.1489	4.2332	6.4593
D	—	—	—	—	—	—	—	—
E	0.01272	0.01265	0.02494	0.02482	0.02938	0.03880	0.02671	0.04076
F	0.0129	0.01264	0.0255	0.0255	0.0300	0.0397	0.0273	0.0419
G	40.04	39.30	63.68	62.05	71.27	78.81	58.20	87.32
H	0.02732	0.02665	0.03874	0.03723	0.04189	0.04001	0.03149	0.04656
K	0.05866	0.05884	0.1303	0.1306	0.1571	0.2230	0.1491	0.2295
L	0.1125	0.1073	0.0900	0.0820	0.0851	0.05142	0.04849	0.0690
R	4.61	4.65	5.22	5.26	5.35	5.75	5.58	5.63
ψ	8.83	8.90	7.81	7.73	7.62	7.17	7.29	7.30

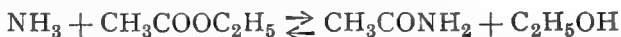
A	9.	10.	11.	12.	13.	14.	15.
B	7.4224	5.811	5.3922	5.6624	3.9716	11.5222	11.0326
C	5.8523	7.6946	9.3930	11.0293	8.6004	—	—
D	—	—	—	—	—	4.4614	6.0886
E	0.03693	0.04855	0.05926	0.06958	0.05423	0.000528	0.000720
F	0.0371	0.0490	0.0610	0.0706	0.0542	—	—
G	74.42	84.35	96.02	109.8	83.43	57.38	63.04
H	0.03749	0.03580	0.03676	0.0402	0.02917	0.05685	0.06232
K	0.2127	0.2933	0.3648	0.4316	0.3386	0.1898	0.2744
L	0.04684	0.03032	0.02452	0.02414	0.01596	0.0741	0.06304
R	5.76	6.04	6.16	6.20	6.24	359.7	381.0
ψ	7.09	6.94	6.62	6.45	6.35	4.35	4.45

No appreciable amount of ethyl chloride is formed under the conditions of the experiments.

The apparent value for the equilibrium constant varies from 4 to over 8 as the concentration of the hydrogen chloride increases.

The apparent diminution in the active mass of the water corresponds nearly with the formation of a compound having the formula $\text{HCl} \cdot 2\text{H}_2\text{O}$, or of compounds having that mean composition.

Another example of equilibrium is afforded by the action of ammonia upon ethyl acetate, acetamide and ethyl alcohol being produced according to the equation—



This has been investigated by Bonz (*Zeitsch. physik. Chem.*, 2, 865, 1888), who showed, however, that the actual process is a more complicated one, for he succeeded in isolating ethyl ammonium acetate, ethyl acetamide, and water, in addition to the above.

A similar sort of difficulty was believed to exist in connection with the action of sulphuric acid upon ethyl alcohol, which on the simplest assumption should correspond to the equation—



The results obtained led Zaitschek (*Zeitsch. physik. Chem.*, 24, 1, 1897) to conclude that the sulphuric acid existed in solution in the form of ortho sulphuric H_6SO_6 . This conclusion is by no means convincing, and recent results of R. Kremann (*Monatshefte*, 31, 245, 1910) go to show that the reaction is the simple one after all, the equilibrium constant—

$$K = \frac{C_{\text{e acid}} \times C_{\text{e alcohol}}}{C_{\text{e ester}} \times C_{\text{e H}_2\text{O}}}$$

having the value 1.74, and this happens to be practically independent of temperature (from 22° C. to 96° C.). The course of the reaction can scarcely yet, however, be regarded as definitely settled. With the exception of the Berthelot and St. Gilles reaction, there are not many instances recorded in the

case of liquid mixtures upon which one can test the law of mass action.

2. SOLUTIONS.

It will be assumed that the reader is familiar with some of the ordinary physical properties of solutions, such as, the phenomena of saturation and super-saturation, diffusion of the dissolved substance or substances from places of high concentration to those of low, distillation and separation of constituents in certain cases by this means, as well as by freezing out part of the solvent, and so producing a more concentrated system. We may, therefore, pass on at once to consider the most important phenomenon exhibited by a solution, namely, the *osmotic pressure* of the solute or dissolved substance.

This is intimately connected with the diffusion or osmosis of the solute, since diffusion from high to low concentration is considered to take place in virtue of the existence of a force which when reckoned per unit area is called osmotic pressure. The earliest account of the phenomenon was given by the Abbé Nollet, who found that if a glass vessel be filled with spirits of wine, the opening tightly covered with a bladder, and the vessel immersed in water, then the volume of the contents of the vessel increases, so that the bladder is expanded and often burst. This experiment was repeated years later by Parrot in 1815, who came to the conclusion that all miscible liquids show a tendency to wander the one into the other, when they are brought into contact, and this process continues until the liquids are perfectly evenly distributed. For many years experiments were always made with animal membranes, until in 1867, Moritz Traube (*Archiv. f. Anat. und Physiol.*, p. 87) showed how chemical membranes could be made in the laboratory by precipitation. Traube showed that certain dissolved substances are able to pass through these membranes, whilst other substances cannot, but Traube did not measure the pressure effects produced by the phenomenon. Pfeffer, in 1877 (*Osmotische Untersuchungen*, Leipzig), was the first to carry out measurements of osmotic pressure. His apparatus

consisted of a porous clay vessel, the walls of which served to support a precipitate of copper ferrocyanide—the precipitate is obtained embedded in the walls of the cylinder by placing a solution of potassium ferrocyanide inside and copper sulphate solution outside, and allowing both to diffuse into the walls, the precipitate being formed at the surface of contact. A cell of this kind allows water to pass freely through it, but prevents many dissolved substances, such as cane sugar in water. The arrangement is represented diagrammatically in the figure (Fig. 22). The cell is filled quite full with the solution of known strength, a manometer attached, and then immersed in pure water. It is found that water

passes into the cell, thereby causing an increase in the pressure as indicated by the rise of mercury in the longer limb of the manometer. This goes on to a certain point until equilibrium is reached, at which the pressure¹ exerted downwards prevents any further water passing into the cell—more correctly, at this stage just as much water enters as leaves the cell per second. Very large pressures are often indicated, sometimes amounting to many atmospheres. The noteworthy fact in this connection is

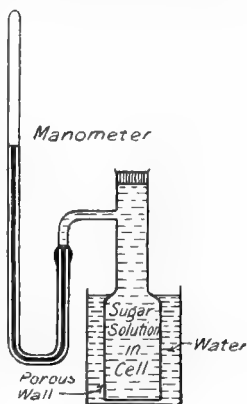


FIG. 22.

that the pressure registered, P , when equilibrium is attained depends on the concentration of the solute, being, according to Pfeffer, directly proportional to the concentration, provided the solution is not too strong. That is to say, that $\frac{P}{c} = \text{constant}$,

an expression which is quite analogous to Boyle's Law for gases. Pfeffer also observed that P varies directly as the absolute temperature, this behaviour being analogous to the Gay-Lussac-Charles Law. Further, it was observed that in many cases, *i.e.* when the solutes were non-electrolytes, the osmotic pressures produced by equimolecular concentrations of different

¹ Hydrostatic pressure due to the column of liquid water.

substances were the same, indicating that Avogadro's principle was also applicable to dissolved substances. The laws of osmotic pressure are so important from the standpoint of the theory of solutions, that it is necessary to give some more detailed account of them, and in this connection the best method will be to quote a number of passages from a paper published by the late Prof. J. H. van 't Hoff, which appeared in Germany in 1887, summarising the results given in a number of papers presented to the Swedish Royal Academy of Sciences, in October, 1885. The English translation of this classical paper appeared in the *Philosophical Magazine* 1888, where it is easily accessible to English readers. For the present we must restrict ourselves to the experimental side only. The thermodynamic treatment of the subject, which formed probably the most striking feature of van 't Hoff's work, must be postponed.

"During an investigation which required some knowledge of the laws regulating chemical equilibrium in solutions, the conclusion has gradually been evolved that a deep analogy—indeed, almost an identity—exists between dilute solutions exerting osmotic pressure on the one hand, and gases under ordinary atmospheric pressure on the other. The following pages contain an attempt to explain this analogy, and the physical properties of such systems will form the first subject of discussion.

"Osmotic Pressure—the nature of the analogy due to this conception.

"In order clearly to realise the quantity referred to as osmotic pressure, imagine a vessel A (Fig. 23) completely

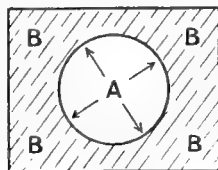


FIG. 23.

full of an aqueous solution of sugar, placed in water B. If it be conceived that the solid walls of this vessel are permeable to water, but impermeable to the dissolved sugar, then, owing to the attraction of the solution for water, water will enter the vessel A up to a certain limit, thereby increasing the pressure on the walls of the vessel [inside].

Equilibrium then ensues owing to the pressure resisting further entry of the water. This

pressure we have termed *osmotic pressure*. It is evident that this state of equilibrium might have been attained in A without entry of water if the vessel had been constructed with a piston compressing the solution with a pressure equal to the osmotic pressure (Fig. 24). It follows moreover that by increasing or diminishing the pressure on the piston the state of concentration of the liquid [solution] can also be altered owing to the passage of water through the walls of the vessel in an outward or inward direction.

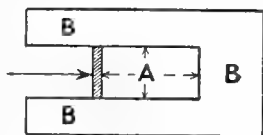


FIG. 24.

Such osmotic pressure has been experimentally investigated by Pfeffer [*l.c.*].” We are already familiar with his experimental arrangement. “As an example of the results obtained it may be mentioned that a one per cent. solution of sugar (which, owing to its considerable mass, was not appreciably diluted on entry of water) exerted at 6.8° C. a pressure of 50.5 mm. mercury—about $\frac{1}{15}$ th atmosphere. The porous membrane such as that described will be termed in the following pages a ‘semi-permeable’ membrane; and the conception will be made use of even when experimental verification is lacking. The behaviour of solutions may thus be studied in a manner strictly analogous to that employed in the study of gases, inasmuch as what is known as ‘osmotic pressure’ corresponds to the pressure, or as it is commonly but incorrectly termed, the ‘tension’ of a gas. It is right to mention that this is no fanciful analogy, but a fundamental one.” Van ’t Hoff restricts his conclusions to *ideal solutions*, that is to say, solutions so dilute that the action of the dissolved molecules upon one another, as well as their actual volume compared with that of the space they inhabit, is so small as to be negligible; that is to say, an ideal solution is analogous to an ideal gas. In practice, of course, we can only work—even in the most dilute cases—with approximation to this ideal state.

“*Boyle’s Law for Dilute Solutions.*—The analogy between dilute solutions and gases acquires at once a quantitative form, if it be noted that in both cases alteration of concentration

exercises a similar influence on pressure, and is in both cases proportional to the pressure. This proportionality, which for gases goes by the name of Boyle's Law, may be proved experimentally for liquids [*i.e.* solutions] as well as deduced theoretically.

"[*Direct*] *Experimental proof.* (Determination of osmotic pressure for solutions of various concentrations.)

"Let us first adduce Pfeffer's determinations (*l.c.*, p. 71) of the osmotic pressure P in sugar solutions at [approximately] the same temperature (13.2° to 16.1° C.) and with varying concentration c .

c .	P .	$\frac{P}{c}$.
1 per cent.	535 mm.	535
2 "	1016 "	508
2.74 "	1518 "	554
4 "	2082 "	521
6 "	3075 "	513

The approximately constant quotients $\frac{P}{c}$ point conclusively to this proportionality between pressure and concentration.

"*Comparison of Osmotic Pressures by Physiological Methods.*
 —"Observations of de Vries (*Eine methode zu Analyse der Turgorkraft*, Pringsheims Jahrbuch 14) show that equal changes of concentration of solutions of sugar and of potassium sulphate and nitrate exercise equal influence on the osmotic pressure. This osmotic pressure was compared, by physiological methods, with that of the contents of a plant cell; the protoplasmal envelope contracts when it is immersed in solutions possessing great attraction for water. By a systematic comparison of the three bodies mentioned, using the same cells, three *isotonic liquids* (*i.e.* liquids [solutions] exhibiting the same osmotic pressure) were obtained. Cells of a *different* plant were then made use of, and so four isotonic series were constructed [by the help of four different plant cells] which showed a similar proportion in their concentrations;

this is exhibited in the following table, where the concentrations are expressed, first in gram-molecules per liter, and then referred to potassium nitrate as unity."

Series.	KNO_3 .	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$.	K_2SO_4 .	$\text{KNO}_3=1$.	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$.	K_2SO_4 .
I.	0.12	—	0.09	1	—	0.75
II.	0.13	0.2	0.1	1	1.54	0.77
III.	0.195	0.3	0.15	1	1.54	0.77
IV.	0.26	0.4	—	1	1.54	—

If van 't Hoff's idea held quite generally for all dissolved substances, one would have expected that the second half of the table would simply consist of a series of the same number, namely, one.

Reasons for the discrepancy—which is *not* due to inherent error in van 't Hoff's conception—will be given when we come to study electrolytic dissociation. The above results show, however, that the effects are independent of the nature of the membrane, since different plant cells were employed, and this is in agreement with van 't Hoff's view.

Theoretical Proof.—"These observations render highly probable the existence of proportionality between osmotic pressure and concentration, and the theorem may be completed by a theoretical proof which is indeed almost self-evident." "Regarding osmotic pressure as due to a kinetic cause (*i.e.* as produced by impacts of the dissolved molecules [upon the inside of the semi-permeable membrane]), there must exist a proportionality between the number of impacts in unit time and the number of molecules in unit volume. The proof is therefore exactly the same as that for Boyle's Law." "If, on the other hand, osmotic pressure be regarded as the outcome of an attraction for water molecules, its value is evidently proportional to the number of attracting molecules in unit volume, provided (and this is taken for granted in sufficiently dilute solutions) the dissolved molecules exercise no attraction on each other, and each one exerts its own special attractive action uninfluenced by its neighbours."

Such a view would equally lead to the conclusion that a law analogous to that of Boyle should hold for dilute solutions. For a long time there was considerable controversy regarding the actual mechanism of osmotic pressure. At the present time the view seems to have gained ground that the effect is very probably the simple kinetic one suggested first by van 't Hoff. Granted that such a force is acting outwards (provided the solution be placed *inside* the porous pot and semi-permeable membrane), it is clear that the solution tends to increase in volume, and this it can do if the opportunity be given for water to stream in from the outside through the membrane. By this process the solution tends to dilute itself, *i.e.* the *water* concentration tends to become identical on both sides of the membrane. If there were no membrane present, or if the membrane were equally permeable to solute and solvent, the solute would diffuse out until finally the whole system would be equally concentrated with respect to solute, and therefore equally concentrated with respect to solvent. It seems reasonable to suppose, therefore, that when diffusion of a solute does occur in a given direction, it is due to the osmotic (kinetic) pressure acting as the driving force. Of course we cannot speak of the osmotic pressure of the solvent, but simply of the solute, since the concentration of the solute corresponds to gas concentration.

“*Gay-Lussac's Law for Dilute Solutions.*—While the proportionality between concentration and osmotic pressure is self-evident so long as the temperature remains constant, the proportionality between osmotic pressure and absolute temperature, the concentration being maintained constant, is not so manifest. Yet proof can be furnished from thermodynamic considerations; and experimental data exist which are highly favourable to the results predicted on thermodynamic grounds.

“*Experimental Proof.* (Determination of the osmotic pressure at different temperatures.)—Pfeffer (*l.c.*, pp. 114–115) found that the osmotic pressure increases with rise in temperature. It will be seen that although his results do not furnish a conclusive proof of the correctness of the theorem, yet there

is a most striking correspondence between experiment and theory. If we calculate from one of two experiments at different temperatures the osmotic pressure to be expected in the other by the help of Gay-Lussac's Law and compare it with the experimental result, we have the following series :—

I. Solution of cane sugar.

Pressure at 32° C. found . .	544 mm.
Pressure at 14·15° C. calculated	512 „
„ „ „ found . .	510 „

II. Solution of cane sugar.

Pressure at 36° C. found . .	567 „
Pressure at 15·5° C. calculated	529 „
„ „ „ found . .	520·5 „

III. Solution of sodium tartate.

Pressure at 36·6° C. found . .	1564 „
Pressure at 13·3° C. calculated	1443 „
„ „ „ found . .	1431·6 „

IV. Solution of sodium tartate.

Pressure at 37·3° C. found . .	983 „
Pressure at 13·3° C. calculated	907 „
„ „ „ found . .	908 „

“*Comparison of the Osmotic Pressure by Physiological Methods.*—In the same manner that support has been lent to the application of Boyle's Law to solutions (viz. that different substances in *isotonic* solutions retain their equality of osmotic pressure, so long as their respective concentrations are reduced to the same fraction), so the application of Gay-Lussac's Law receives support by the fact that this isotonic state is maintained during equal alterations of temperature. It has been proved by physiological methods by Donders and Hamburger (*Onderzoekingen gedaan in het physiol. Laborator. der Utrechtsche Hoogeschool*, [3] 9, 26), making use of blood corpuscles, that solutions of potassium nitrate, sodium chloride, and sugar, which at 0° C. are isotonic with the contents of these cells, exhibit the same isotonic state at 34° C.; this is seen in the annexed table :—

	Temperature 0° C.	Temperature 34° C.
KNO ₃	1'052—1'03 per cent.	1'052—1'03 per cent.
NaCl	0'62 —0'609 „	0'62 —0'609 „
C ₁₂ H ₂₂ O ₁₁	5'48 —5'38 „	5'48 —5'38 „

“ *Experimental proof of Boyle's and Gay-Lussac's Laws for Solutions.*—Experiments by Soret (*Archives des sciences phys. et nat.*, [3] ii., p. 48; *Annales de Chim. et de Phys.*, [5] 22, 293).

“ The phenomenon observed by Soret lends a strong support to the analogy between dilute solutions and gases in respect of the influence of concentration and temperature on pressure. His work shows that just as in gases the warmest part is the most rarefied, so with solutions the warmest portions are the most dilute; but that in the latter case a much longer time must be allowed for the attainment of equilibrium. The experimental apparatus consisted of a vertical tube, the upper portion of which was heated while the lower portion was kept at a low temperature.

“ Soret's latest experiments lend a quantitative support to our analogy. As with gases, it is to be expected, that when the isotonic state is produced the solution will exist in equilibrium; and as the osmotic pressure is proportional to concentration and absolute temperature, the isotonic state of different portions of the solution will occur when the products of the two (absolute temperature and concentration) are equal. If we therefore calculate on this basis the concentration of the warmer part of the solution from data obtained from the colder, the values compare with those found as follows:—

“ 1. Solution of copper sulphate. The portion cooled to 20° C. contained 17'332 per cent. The hot portion at 80° C. should contain 14'3 per cent.; found 14'03 per cent.

“ 2. The portion cooled to 20° C. contained 29'867 per cent. The portion at 80° C. should contain 24'8 per cent.; found 23'871 per cent.

It must be stated that previous experiments by Soret gave less favourable results; yet perhaps too much importance should not be attached to them, owing to the difficulties of

experiment." In addition to the experimental evidence cited by van 't Hoff, mention may be made of an optical method of determining isotony of solutions by Tammann (*Wied. Ann.*, **34**, 299, 1888). The method is based on the use of the Töpler apparatus for detecting small changes in the refractive powers of liquids or solutions. A Pfeffer cell is set up containing a solution of some substance inside and immersed in a solution of another substance outside. If the concentrations are such that the solutions are isotonic, no solvent will pass from one side to the other. If the solutions are not isotonic, solvent will pass either inward or outward, causing thereby a change in concentration or "streaming" near the wall which can be detected by the change in the refractive index. It is thus possible to adjust one liquid to the other in respect of concentration of solute so that no change in refractive index is observed. Tammann used copper ferrocyanide and zinc ferrocyanide membranes. He compared copper salts and zinc salts against potassium ferrocyanide. In the following table are given data which show that the *ratio* of the isotonic concentrations does not change much with increasing dilution. On van 't Hoff's assumption it should not change at all as long as the solutions in all cases may be described as dilute.

Isotonic solutions. Concentration in gram-molecules per 1000 grams H ₂ O.		Ratio $\frac{\text{Concentration of CuSO}_4}{\text{Concentration of K}_4\text{Fe(CN)}_6}$
CuSO ₄ .	K ₄ Fe(CN) ₆ .	
0.842	0.313	2.7
0.675	0.240	2.8
0.339	0.117	2.9
0.204	0.079	2.6
0.170	0.066	2.6
0.094	0.036	2.6

The method can be further extended by adding to one of the solutions, say the CuSO₄, some third substance and then finding what concentration of ferrocyanide is isotonic with the mixed solution. That part of the osmotic pressure which is due to

the substance added can then be calculated on the supposition (the accuracy of which it would be possible to establish by the experiments themselves), that the osmotic pressure of the mixed substances is the sum of the pressures of each, *i.e.* Dalton's Law.

Avogadro's Hypothesis applied to Dilute Solutions.—Avogadro's hypothesis states that one mole of a gas at a given temperature and pressure occupies the same volume as one mole of any other gas at the same temperature and pressure, provided, of course, that abnormal effects such as dissociation are absent. Having found that Boyle's and Gay-Lussac's Laws hold for dilute solutions, van 't Hoff was led to the assumption that Avogadro's hypothesis would likewise hold for dilute solutions, *i.e.* under equal osmotic pressures and at the same temperature equal volumes of different solutions would contain equal numbers of solute molecules, or equimolecular solutions at the same temperature should exert the same osmotic pressure; and further, if a solution exerts an osmotic pressure, say, of P atmospheres at a given temperature, there are just as many *solute* molecules in a given volume of the solution as there would be gas molecules in the same volume of gas, supposing the gas also exerted P atmospheres pressure at the above temperature.

The well-known formula expressing both Boyle's and Gay-Lussac's Laws for gases—

$$pv = RT$$

is, in so far as these laws are applicable to liquids [solutions], also applicable as regards osmotic pressure; with the reservation, also made in the case of gases, that the space occupied by the molecules must be so great that the actual volume of the molecules becomes negligible. If Avogadro's hypothesis be also introduced, it may be expressed in the above equation by giving to R a certain numerical value, namely, 1.98 (or 2.0 approximately), the unit of energy being the calorie, the unit of mass of gas considered being one mole. It is to van 't Hoff that we owe the idea that this gas equation is directly applicable to solutions, the value of R being identical with its value for gaseous bodies.

“First Confirmation of Avogadro’s Hypothesis in its application to Solutions—Direct Determination of Osmotic Pressure.—It is to be expected that Avogadro’s hypothesis deduced as a consequence of Henry’s Law for solutions of gases, will not be restricted to solutions of substances which usually exist in a gaseous condition. This expectation has been realised, not merely from a theoretical, but from an experimental standpoint. Pfeffer’s determinations of the osmotic pressure of solutions of sugar furnish a remarkable proof of this extension of the hypothesis.

“Pfeffer’s solution consisted of 1 gram of sugar dissolved in 100 grams of water; 1 gram of the sugar therefore exists in about 100.6 c.c. of the solution.”

The number of moles of sugar in 100.6 c.c. is therefore $\frac{1}{342}$ (since $C_{12}H_{22}O_{11} = 342$). The concentration is therefore $\frac{1 \times 1000}{342 \times 100.6}$, or 0.02906 mole per liter. Let us now calculate what pressure would be exerted by hydrogen gas, say (molecular weight 2), at $0^{\circ}C$. and at the above concentration. One litre of hydrogen gas weighs 0.08956 gram at $0^{\circ}C$. when its pressure is one atmosphere. That is, its concentration in moles per liter is $\frac{0.08956}{2}$, or 0.04478. Since gas pressure is proportional to concentration, it is evident that at a concentration of 0.02906 mole per liter the hydrogen would only exert a pressure of $\frac{0.02906}{0.04478}$, or 0.649 atmosphere at $0^{\circ}C$. Similarly, at any temperature t the pressure will be $0.649(1 + 0.00367t)$. Placing these results beside Pfeffer’s, we obtain the following agreement:—

Temp. t .	Osmotic pressure.	Gas pressure under same conditions. $0.649(1 + 0.00367t)$.
6.8	0.664	0.665
13.7	0.691	0.681
14.2	0.671	0.682
15.5	0.684	0.686
22.0	0.721	0.701
32.0	0.716	0.725
36.0	0.746	0.735

The directly determined osmotic pressure of a solution of sugar is thus seen to be equal to the pressure of a gas at the same temperature, containing the same number of molecules in unit volume as the sugar solution.

“Starting from cane sugar, this relation can be calculated for other dissolved substances, such as invert sugar, malic acid, tartaric acid, citric acid, magnesium malate and citrate, all of which from de Vries’ physiological researches (*Eine Methode zur Messung der Turgorkraft*) exhibit equal osmotic pressure, when they contain an equal number of molecules in a given volume.”

Besides the evidence for the applicability of the gas laws cited by van ’t Hoff, one may mention Tammann’s results (*l.c.*), in which it was found that in aqueous solutions of cane sugar, salicin, ethyl alcohol, urea, propyl alcohol, equimolecular solutions possessed the same osmotic pressure within the limits of experimental error. Tammann further pointed out that solutions with the same osmotic pressure possess the same vapour pressure—a statement which we shall come to presently in van ’t Hoff’s paper.

The most accurate verification of the applicability of the gas laws to dilute solutions at various temperatures is furnished by the work of Morse and Frazer and their collaborators (*Journ. Amer. Chem. Soc.*, 1907–1912). In the work of 1908 the osmotic pressures of aqueous solutions of sucrose were determined at 10° C. and 15° C., solutions of dextrose at 20° C. Considerable difficulty was met with in the preparation of satisfactory semi-permeable membranes, and the success of the work really lay in overcoming this. The results are accurate to the first place of decimals. Previous measurements had led to the belief that the osmotic pressure at 0° C. was substantially the same as at 20° C., but it was shown in the paper referred to that there is undoubtedly a temperature coefficient of osmotic pressure, and that this coefficient is practically identical with the temperature coefficient of gases. This work is especially remarkable for the elaborate care with which it was carried out, and consequently the trustworthiness of the results, some of which are here tabulated.

OSMOTIC PRESSURE OF SUCROSE SOLUTIONS.

Concentration (weight normal, <i>i.e.</i> gram-molecules of solute per 1000 grams of solvent).	Temperature.			
	0° C.	4° to 5° C.	10°.	15°.
	atmos.	atmos.	atmos.	atmos.
0.1	2.42	2.40	2.44	2.48
0.2	4.79	4.75	4.82	4.91
0.3	7.11	7.07	7.19	7.33
0.4	9.35	9.43	9.58	9.78
0.5	11.75	11.82	12.00	12.29
0.6	14.12	14.43	14.54	14.86
0.7	16.68	16.79	17.09	17.39
0.8	19.15	19.31	19.75	20.09
0.9	21.89	22.15	22.28	22.94
1.0	24.45	24.53	25.06	25.42
Mean "molecular osmotic pressure," <i>i.e.</i> pressure due to one mole solute per 1000 grams solvent.	23.95	24.12	24.50	24.98
Mean "molecular gas pressure," <i>i.e.</i> pressure due to one mole of gas in a volume equal to that occupied by 1000 grams of water at the temperature in question.	22.29	22.65	23.09	23.50
Ratio : mean osmotic pressure to gas pressure.	1.074	1.065	1.061	1.064

If van 't Hoff's assumptions held rigidly, the ratios just given should be unity. Though not unity, they are at least constant.

In 1909 the experiments at 20° and 25° C. were published. The values of the ratio, mean osmotic pressure to gas pressure, were 1.069 at 20° C. and 1.064 at 25° C.

The results obtained more recently ¹ (1912) show that the 0.1 N solution between 30° C. and 60° C., and the 0.2 N solution between 50° C. and 60° C. obeys Gay-Lussac's Gas Law *strictly*.

¹ H. N. Morse, W. H. Holland, C. N. Myers, G. Cash, J. B. Zinn, *Amer. Chem. Journ.*, **48**, 29, 1912.

It has already been mentioned that the ratio of mean osmotic to gas pressure, which should be unity if Boyle's Law held at the same time, is a little larger than unity. This tends, however, towards and eventually becomes unity at higher temperatures, *i.e.* the solutions at higher temperatures become more "ideal." Boyle's Law, for example, holds *exactly* in the following cases :—

Up to 0.2 N solutions at 50° C.	
„ 0.4 N „ 60° C.	
„ 0.7 N „ 70° C.	
„ 1.0 N „ 80° C.	

The work carried out by Morse and his collaborators may be regarded as completely satisfactory proof that dilute solutions do obey the gas laws. Investigation upon more concentrated solutions has shown, on the other hand, that the simple gas laws do not hold at all accurately just as they do not hold for highly compressed gases.

We have been considering the direct evidence for van 't Hoff's assumption regarding the applicability of the gas laws (including the Avogadro hypothesis) to solutions. The next point taken up by van 't Hoff is the "*Second confirmation of Avogadro's hypothesis in its application to solutions. Molecular lowering of vapour pressure.*" We must digress a little at this point in order to consider some of the experimental results obtained in connection with the lowering of the vapour pressure.

It was known for many years that water which contains some non-volatile substance dissolved in it boils at a higher temperature than pure water. The boiling point is simply the temperature at which the vapour pressure of the liquid is equal to atmospheric pressure ; and since the vapour pressure always increases with rise of temperature, the existence of a raised boiling point (in the case of a solution) indicates that the presence of the solute has lowered the vapour pressure of the solvent. The first generalisation made in this connection is that of von Babo (1848), who found that the relative lowering

of vapour pressure, namely, $\frac{p_0 - p_1}{p_0}$ [where p_0 is the vapour pressure of the pure solvent at a given temperature, and p_1 the vapour pressure of a solution (having the same solvent, of course) at the same temperature] is independent of the temperature provided the solution is dilute.

Wüllner (*Poggendorff's Ann.*, 103, 529, 1858; 105, 85; 110, 56, 1860) came to the conclusion that the lowering of the vapour pressure of water by non-volatile solutes is proportional to the concentration of the solute. The later work of Tammann showed that the law of proportionality was not strictly accurate. It is important to note that the substances examined by these investigators were salts, *i.e.* electrolytes, in aqueous solution. A great deal of apparent contradiction and lack of uniformity was removed, however, when Raoult¹ commenced his classic work on the behaviour of non-electrolytes, organic substances, dissolved in organic solvents. Raoult employed the barometric method for determining the vapour pressure.

Employing ether as solvent, Raoult was able to confirm von Babo's Law, namely, that the fractional lowering of vapour pressure $\frac{p_0 - p_1}{p_0}$ is independent of the temperature. He also found that for solutions of medium concentration the fractional lowering of vapour pressure is proportional to the concentration—which is Wüllner's Law. The most important advance, however, made by Raoult lay in the introduction of the "molecular lowering" of vapour pressure, *i.e.* he compared the lowering produced by equimolecular quantities of different solutes in the same solvent. If M is the molecular weight of the solute, x the mass of solute in grams dissolved in 100 grams of ether, then the "molecular lowering" c_1 was found to be a constant for the solvent employed, namely, ether. c_1 is given by the expression—

$$c_1 = \frac{p_0 - p_1}{p_0} \cdot \frac{M}{x}$$

¹ *Comptes Rendus*, 103, 1125, 1886. The work was actually begun in the 'seventies and continued for a number of years without publication.

The following table contains some of Raoult's data (solvent ether):—

Solute.	M.	c_1 .
Carbon hexachloride .	237	0·71
Turpentine . . .	136	0·71
Methyl salicylate .	152	0·71
Cyanic acid . . .	43	0·70
Benzoic acid . . .	122	0·71
Trichloroacetic acid .	163·5	0·71
Benzaldehyde . . .	106	0·72
Caprylic alcohol . .	130	0·73
Cyanamide	42	0·74
Aniline	43	0·71
Antimony trichloride .	228·5	0·67

Some of these solutes scarcely correspond to the condition of non-volatility even at ordinary temperatures—the solvent ether happened to have a considerable vapour pressure in comparison, however. The molecular lowering of vapour pressure, *i.e.* the lowering produced by one mole of any solute in a given amount of solvent is independent of the nature of the solute. The lowering of the vapour pressure depends therefore on the number of solute molecules present, not on the kind of molecule. When, however, aqueous solutions of salts are examined, one no longer obtains a constant as in the above, unless, indeed, we compare salts of closely analogous type, *e.g.* CuSO_4 , ZnSO_4 , etc., in which case an approximate constant is obtained having a different numerical value from that given above. This circumstance no doubt prevented earlier observers from arriving at Raoult's generalisation. Raoult also discovered the following relationship in 1887 (*C. R.*, 104, 1430), that the lowering of vapour pressures of different *solvents* is the same when the ratio of the number of molecules of solute to molecules of solvent is the same.

In connection with the "molecular lowering" mentioned above it will be well to give at least one instance of the results obtained by Raoult (*Zeitsch. physik. Chem.*, 2, 353, 1888) as evidence of the same law put in a slightly different form. Thus if n is the number of solute molecules dissolved in N

molecules of solvent, then the concentration of the solute molecules expressed as a fraction of the total molecules present may be written $\frac{n}{N+n}$, which for dilute solutions (N large compared to n) may be expressed as $\frac{n}{N}$. If k be the constant of proportionality between the fractional lowering of vapour pressure and the concentration as above expressed, we have the relation—

$$\frac{p_0 - p_1}{p_0} = k \frac{n}{N+n}$$

Raoult determined in this way the value of k experimentally, and then made use of this to calculate the lowering of vapour pressure for a series of concentrations. The agreement between “calculated” and “observed” values is shown in the following table, in which the solute is aniline and the solvent ether :—

$\frac{n}{N+n}$	$100 \frac{p_0 - p_1}{p_0}$		$\frac{n}{N+n}$	$100 \frac{p_0 - p_1}{p_0}$	
	observed.	calculated.		observed.	calculated.
3.85	4.0	3.4	20.5	19.7	18.4
7.7	8.1	6.9	49.6	42.4	44.6
14.8	15.4	13.3	68.7	59.6	61.8

The relationship discovered by Raoult may be used to determine the molecular weight of the solute, assuming the molecular weight of the solvent is known. That is, if a certain mass of solution is known to contain N moles of solvent, we can calculate n if we already know the k for the solvent¹ and determine the lowering of vapour pressure. If m grams of solute are actually present and M is its molecular weight in

¹ This in turn must have been obtained from data obtained with a solute the molecular weight of which was known, *i.e.* one whose molecular weight corresponds to the smallest value which would be in agreement with the composition of the substance given by analysis. The values are therefore strictly *relative* only.

solution, evidently $n = \frac{m}{M}$, whence M can be calculated. As a matter of fact, the method of measurement of lowering of vapour pressure has been very little used for the determination of molecular weights until recently Menzies has improved the technique (see Part II. (Vol. II.), Chap. VI.). The usual methods for molecular weight determination are those which are closely allied to the lowering of vapour pressure on theoretical grounds, namely, the "lowering of freezing point" and the "rise of boiling point" methods.

Returning to van 't Hoff's argument, it will be remembered that he considers the numerical data obtained in the case of the "molecular lowering of vapour pressure" as the second confirmation of the application of Avogadro's law to solutions. He does this by showing by means of thermodynamics the relationship which must exist between the osmotic pressure of

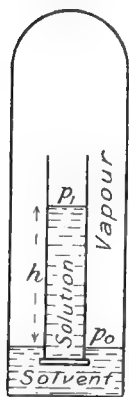


FIG. 25.

the solution (*i.e.* of the solute in the solution) and the lowering of vapour pressure of the solvent owing to the presence of the solute. Instead of following the thermodynamical reasoning (which will be taken up in Part II. (Vol. II.), Chap. VI.) we shall consider the problem from the kinetic standpoint by a method first proposed by Arrhenius in 1889 (*Zeitsch. physik. Chem.*, **3**, 115, 1889). Suppose we have a tube¹ having a semi-permeable membrane fixed at the lower end and partly filled with a solution of cane sugar in water, the tube dipping into pure water as shown in the figure (Fig. 25). Water enters the tube until the solution forms a column of height h . Suppose equilibrium is attained at that point, *i.e.* suppose

that the hydrostatic pressure of the column of solution which tends to drive solvent downwards through the membrane just balances the osmotic pressure P of the solution which has

¹ The tube is not a capillary one, nor is the surface of the solution curved as in the case of the somewhat similar arrangement due to Lord Kelvin for the determination of the change of vapour pressure of a pure liquid with curvature.

caused the entry of water upwards. Let ρ be the mean density of the solution, this being practically the density of the solvent if the solution is dilute. Let σ be the mean density of the vapour over the range h . In the actual case the density of the vapour alters with the height. We are dealing with a simplified case which is only approximately true. Let p_0 be the value of the vapour pressure over the solvent and p_1 that over the solution. The hydrostatic pressure of the liquid column acting downwards is $h\rho g$. At the equilibrium this is balanced by P . That is—

$$P = h\rho g.$$

But considering an imaginary column of vapour also of height h , the hydrostatic pressure of the vapour is $h\sigma g$ and this must be identical with the difference of the vapour pressures at the top and bottom of the column, namely, $p_0 - p_1$.

Hence

$$h - h - h - h$$

ERRATA

Page 211, line 9 from top, in place of $h\rho$ insert $h\rho g$

"	"	11	"	"	"	"	"
"	"	13	"	"	$h\sigma$	"	$h\sigma g$
"	"	16	"	"	"	"	"

Since at a given (constant) temperature ρRT is constant (as long as the different solutions do not vary too much in concentration, *i.e.* as long as their densities are approximately that of the solvent), one may write—

$$\frac{p_0 - p_1}{p_0} \propto P$$

i.e. the fractional lowering of vapour pressure is proportional to the osmotic pressure. Now van 't Hoff's theory may be expressed in the equation—

$$P = RTc$$

where c is the concentration of the solute or the reciprocal of the dilution. c expressed, say, in moles per litre is proportional to $\frac{n}{N+n}$.

Hence
$$\frac{p_0 - p_1}{p_0} = \frac{RTc}{\rho RT} = \frac{c}{\rho}$$

and since ρ is a constant, approximately, under the conditions specified, we can see that the fractional lowering of vapour pressure is proportional to the concentration c , or proportional to $\frac{n}{N+n}$, which is Raoult's Law. The fact that the application of Avogadro's hypothesis to dilute solutions permits of the deduction of Raoult's experimental relation, is evidence for the applicability of the hypothesis.

As already mentioned, closely connected with the phenomenon of the lowering of vapour pressure is that of the "elevation of boiling point." The elevation is directly proportional to the lowering of the vapour pressure, and since it has been found fairly easy to make accurate determinations of changes in boiling point by Beckmann's method, this may be used to calculate the molecular weight of the dissolved substance. In this phenomenon, the application of Avogadro's hypothesis leads to the statement that equi-molecular concentrations of various solutes in the same solvent cause the same elevation of boiling-point. This has been verified experimentally, and may be likewise deduced on thermodynamic grounds. The discussion of the deduction and its use in the determination of molecular weight must be postponed.

We now pass on to van 't Hoff's "*third confirmation of Avogadro's Law in its application to solutions. The molecular depression of freezing-point of the solvent,*" due to the presence of the solute. We shall look for a moment at some of the earlier researches. The earliest investigation of the subject was carried out by Blagden in 1788 (*Phil. Trans. Roy. Soc.*, 78, 277), who showed that the depression of freezing point of aqueous solutions of a given substance below the freezing point of water was proportional to the concentration of the

substance in solution. Blagden's work did not attract any attention. His generalisation was rediscovered independently by Rüdorff in 1861, but it was only in 1871 that attention was drawn by Coppet to the earlier work. In the case of the solutions thus investigated, and those which we are about to mention in more detail, it is important to remember that when freezing takes place it is the pure solid solvent which crystallises out. This is likewise the case considered by van 't Hoff. If the solute separates out simultaneously with solvent to form a *homogeneous* mass called a "solid solution," or "mixed crystal," or, on the other hand, if solvent and solute separate out to give a heterogeneous conglomerate (crystals of both lying side by side), such being known as a cryohydric mixture, we can no longer—on theoretical grounds—expect the simple relationship to hold. For the verification of the van 't Hoff assumption we must deal only with those solutions from which pure solvent separates out on freezing. It happens that this includes by far the larger number of cases so far investigated. It should be mentioned that the work of Coppet and Rüdorff referred to, while supporting Blagden's general conclusion, also brought to light many examples of apparently abnormal behaviour, *e.g.* in the case of strong acids, bases, and salts in aqueous solution, which served to show that the phenomenon was rather a complicated one, and it was not until the theory of electrolytic dissociation was put forward by Arrhenius (1883) that an explanation of many of these abnormalities was forthcoming. The work of Raoult, begun several years previously and published in 1882 (*Compt. Rend.*, **94**, 1517, 1882; *ibid.*, **95**, 188, 1030, 1882), in which organic substances were employed as solutes in aqueous solution, served to bring out the important relationship that the "*molecular depressions of freezing point were nearly the same for the various solutes when dissolved in one and the same solvent, e.g. water.*" Raoult extended his investigations to other solvents, and again obtained a series of new constant molecular depressions. (Raoult had also noticed certain abnormalities in the case of water when this was the solvent.) The results of his work were published in detail in the *Annales de Chim. et de Physique*, [5] **28**, 137, 1883; *ibid.* [6] **2**, 66, 1884.

Defining the molecular depression of freezing point as the lowering produced by one gram molecular weight (one mole) of the solute in 100 grams of solvent, we find that the following data (taken from the very extended tables given by Raoult, bear out his statement :—

SOLUTIONS IN BENZENE.		SOLUTIONS IN WATER.	
Solute.	Molecular depression.	Solute.	Molecular depression.
Methyl iodide . . .	50.4	Urea	17.2
Nitrobenzene . . .	48.0	Acetamide	17.8
Naphthalene . . .	50.0	Ethyl acetate . . .	17.8
Anthracene	51.2	Tartaric acid . . .	19.5
<hr/>		Acetic acid	19.0
Ethyl alcohol . . .	28.2	Cane sugar	18.5
Methyl alcohol . . .	25.3	Ethyl alcohol . . .	17.3
Phenol	32.4	<hr/>	
Acetic acid	25.3	Hydrochloric acid .	39.1
Benzoic acid	25.4	Nitric acid	35.8
		Caustic potash . . .	35.3
		Potassium chloride .	33.6
		Sodium chloride . .	35.1

A glance at the table shows that for one and the same solvent we may divide solutes in respect of molecular depressions of freezing-point into at least two sets—indicated by the dotted lines. An abnormally *small* depression could be brought about by *association* of some of the solute molecules together, for the depression is proportional to the *number* of solute particles present in a given volume, and so, although we may have added a mole of solute in grams, owing to a number of these being associated say to produce molecules of double the normal molecular weight, there are fewer individuals present than we would normally anticipate, and hence the depression produced is abnormally small. This is true, for example, in the case of solutes containing hydroxyl groups, alcohols, acids, etc., or cyanogen groups when dissolved in benzene.¹ On the other hand, abnormally great depression was attributed later by Arrhenius (*Zeitsch. physik. Chem.*, 1887), to electrolytic

¹ This can be shown, for example, by applying Nernst's theory of the distribution of a solute between two immiscible solvents (cf. Chapter VII.).

dissociation, which had suggested itself to him some four years previously, and according to which a molecule of an electrolyte can give rise to two or more electrically charged atoms or ions, *i.e.* individuals are present in greater number than would be normally expected from the mass of substance dissolved, thereby causing the abnormally great depression. This is characteristically the case with inorganic acids, bases, and salts in aqueous solution, such solutions possessing at the same time the property of conducting the electric current, the solute being therefore called an 'electrolyte.' Substances which do not conduct current are known as 'non-electrolytes.' Arrhenius' explanation was, however, necessarily unknown to van 't Hoff when he first brought out his osmotic theory of solution; so that quantitative support to his theory could only be obtained from *some* of Raoult's values, namely, those which are now regarded as 'normal,' in which the solute molecules are neither associated nor dissociated. It is the great merit of Arrhenius' theory of electrolytic dissociation that it offers an explanation of the abnormally great depressions observed with inorganic acids, bases, and salts in aqueous solution, which is in quantitative accord with the osmotic theory of solution.

The striking feature in favour of van 't Hoff's argument as regards the phenomenon of molecular depression, is that he actually calculated by thermodynamic means what the normal constant should be for substances dissolved in a given solvent. The formula obtained by van 't Hoff applies equally well to the molecular rise of boiling-point, provided corresponding meanings are attached to the symbols. The expression referred to may be written—

$$\delta = \frac{0.02T^2}{L}$$

where δ stands for the molecular lowering of freezing point,
or molecular rise of boiling point,

T is the absolute temperature of freezing or boiling of
the solvent,

L is the latent heat of fusion, or latent heat of vaporisation per gram of the solvent.

Van 't Hoff goes on to say : " This theoretical deduction receives ample confirmation from experimental data. The following table exhibits the molecular depression of freezing point experimentally determined by Raoult, along with the values calculated by means of the above formula :—

Solvent.	Freezing point, T° abs.	Latent heat of fusion, L.	δ calculated, i.e. $\delta = \frac{0.02T^2}{L}$.	Molecular de- pression ob- served by Raoult.
Water . .	273	79 cal.	18.9	18.5
Acetic acid .	273 + 16.7	43.2 "	38.8	38.6
Formic acid .	273 + 8.5	55.6 "	28.4	27.7
Benzene . .	273 + 4.9	29.1 "	53	50
Nitrobenzene	273 + 5.3	22.3 "	69.5	70.7 "

This part of the subject has been extended at a later date by Eykman (*Zeitsch. physik. Chem.*, 3 and 4, 1889).

NOTE.—It may be well at this juncture to point out that a connection between lowering of freezing point, rise of boiling point, and depression of vapour pressure had been established prior to van 't Hoff's work, though not upon so general a basis. In 1878 Raoult (*Compt. Rend.*, 87, 167, 1878) showed empirically with regard to 18 salts, which he had examined with respect to their effect on the freezing point and boiling point of the solvent, that the effects were proportional to one another. The relation thus empirically established by Raoult had been deduced theoretically some years before by Guldberg (*Compt. Rend.*, 70, 1349, 1870) by a thermodynamic method. The merit of showing the interconnexion of these phenomena with osmotic pressure rests with van 't Hoff. It should be clearly understood that although we have followed van 't Hoff's paper in which his theory is put forward, we have necessarily restricted ourselves to experimental evidence only. As a matter of fact, however, the great value which attaches to van 't Hoff's work rests on its thermodynamical basis, for although thermodynamics had been introduced into chemistry some years previously by Horstmann (1869), van 't Hoff's conception of osmotic pressure and the application of the laws of thermodynamics to "osmotic work" have laid the foundation of the greater part of physical chemistry as it exists to-day.

Before leaving this part of the subject it is of interest to discuss briefly the application of Avogadro's hypothesis to aqueous solutions of inorganic acids, bases and salts.

The generalisation which van 't Hoff found to hold true for

dilute solutions of numerous substances—principally organic substances—in various solvents may be written—

$$P = RTc$$

where P is the osmotic pressure produced by the solute the concentration of which is c (stated as a rule in moles per liter, or sometimes per 1000 grams of solvent). For inorganic acids, bases, and salts¹ in aqueous solution this simple osmotic law does not hold if we ascribe to R the value it has in the case of gases. P is greater, twice or thrice as great in some cases, as the expression RTc . This has manifested itself in the allied phenomena of lowering of freezing point and rise of boiling point. To get over the difficulty van 't Hoff suggested the inclusion of an empirical factor i , which he regarded in the first instance as a constant. The osmotic law of van 't Hoff for solutions of these substances takes the form $P = iRTc$. The factor i was shown later by Arrhenius, on the basis of the electrolytic dissociation theory, not to be constant but to increase as the concentration of the solute diminishes. The following table contains a few of the data given by Arrhenius in 1888 (*Zeitsch. physik. Chem.*, 2, 496, 1888). They refer to determinations of lowering of the freezing point—denoted by Δt —for since the lowering is proportional to P it is likewise proportional to $iRTc$. When a "normal" solute such as cane sugar is used, *i.e.* one for which $i = 1$, and the simple expression $P = RTc$ holds good, it is easy to calculate what the normal values of Δt ought to be, and the ratio of the observed Δt to the calculated value gives i directly.

SOLUTIONS OF SODIUM CHLORIDE IN WATER.

c in moles per liter.	Δt observed.	i .
0.0467	-0.117°	2.00
0.117	-0.424	1.93
0.194	-0.687	1.87
0.324	-1.135	1.86
0.539	-1.894	1.85

¹ The salts may also contain an organic acid radicle, *e.g.* sodium acetate.

SOLUTIONS OF SODIUM SULPHATE IN WATER.

<i>c</i> in moles per liter.	Δt observed.	<i>i</i> .
0.0280	0.141	2.66
0.0701	0.326	2.46
0.117	0.515	2.33
0.195	0.817	2.21

The important point to note is that these substances, which on being dissolved give rise to solutions with abnormally great osmotic pressure, are electrolytes. This makes us at once suspect that there is some close connection between the two sets of phenomena. This will be taken up in the succeeding chapter. Before going on with the phenomena of electrolytic dissociation, however, it is convenient to briefly discuss one or two instances of reactions between the molecules of the solvent and the molecules of the solute present together in the solution.

In dealing with solutions it has already been said that many of the reactions which occur in them may be treated without special reference to the solvent itself. In some cases, however, the solvent actually plays a definite rôle, though it must be remembered that even where the solvent is not considered it is by no means to be inferred that it is perfectly inert. In general, as a matter of fact, there must be some kind of interaction between solvent and solute, even in cases where it is not easy or even possible to demonstrate it. The type of reaction to be considered at this point is, however, one in which it has been possible to show that the solvent is taking a definite chemical part, although so far the methods employed to investigate this sort of phenomenon have not been particularly fruitful except in certain cases. An instance of these reactions is the formation of molecular hydrates (assuming the solvent to be water), that is, compounds formed between a molecule of the solute and one or more molecules of the solvent. Similarly there is evidence to show that ions (present, say, when an inorganic acid, base, or salt is dissolved in water)

may in certain cases be hydrated. There is likewise the widespread phenomenon of hydrolysis of salts dissolved in water. Reactions involving ions will be considered in the following chapter. For the present we shall only consider by way of illustration,¹ a mixture of ethyl alcohol and water from the standpoint of possible union between the molecules to give compounds. Reference may, first of all, be made to the work of Mendeléef, who determined the density of numerous mixtures of alcohol and water of different percentage composition, and concluded from the irregular nature of the curve as we pass from 100 per cent. water to 100 per cent. alcohol that several complexes, *i.e.* molecular compounds, exist in solution. The work of Jones (*Zeitsch. physik. Chem.*, 13, 419, 1894), however, who carried out a series of freezing-point determinations at various concentrations, afforded no evidence for any complex formation. The variation of other physical properties with composition of the solution or mixture has been employed to try and settle the question. Thus the *viscosity* of alcohol-water mixtures reaches a *maximum* at a point corresponding to the composition $C_2H_5OH, 3H_2O$. Such evidence alone must not be taken, however, as actually proving the existence of the complex $(C_2H_5OH, 3H_2O)$ for we have no *à priori* reason for believing that the formation of a complex will necessarily increase the viscosity, and still more when we take into account the further experimental fact that the *position* of the maximum, *i.e.* the composition of the mixture which possesses maximum viscosity, *varies gradually with the temperature*. Now the criterion of a true compound is that its composition should not show any gradual change with change of conditions, such as temperature and pressure. The results of viscosity measurements afford little conclusive evidence, though they are sufficient to show that the system is behaving in a rather remarkable fashion. More definite are the recent results obtained by Dorochevski and Roshdestwenski (*Journ. Russ. Phys. Chem. Soc.*, 40, 860, 1908), using the electrical conductivity method. They showed that

¹ This subject is treated in a very interesting manner by Arrhenius in his book *Theories of Chemistry*.

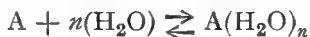
the electrical conductivity passes through a *minimum* (as we alter the concentration progressively) at about 50 per cent. alcohol, and, according to Kohlrausch—who has given reasons for believing that a compound does not conduct so well as a solution—this should really indicate formation of a compound having the composition $(\text{C}_2\text{H}_5\text{OH}, 3\text{H}_2\text{O})$. Of course, an obvious difficulty crops up, in that we are accustomed to regard water and alcohol as non-conductors. This is approximately correct, but they give rise to a few ions. The resistances met with in these Russian investigators' experiments were very large indeed. Mention must also be made of the work of Hess (*Annalen der Physik.*, **27**, 609, 1908), who found that the volume contraction resulting from the addition of alcohol to water showed a maximum at about 50 per cent. water, *i.e.* at a composition corresponding approximately to $(\text{C}_2\text{H}_5\text{OH}, 3\text{H}_2\text{O})$. It is probable, therefore, that this hydrate exists to a very large extent, but the most correct view to take of the whole question is to look upon these complexes as labile compounds, or rather to consider that there are a very large number of different hydrates present, some of which are more stable than others, and exist in larger quantity and therefore affect certain physical properties. These hydrates are in equilibrium with one another at a certain temperature, but with change in this condition there is a corresponding shift in the equilibrium points, so that those which predominate at one temperature may no longer do so at another. It is hopeless, however, to try and apply the principle of mass action to a system so complicated as this.

Another typical instance of complex formation is met with in mixtures of sulphuric acid and water. A study of the physical behaviour of this system, in spite of much conflicting evidence, has yielded the result that the hydrates $(\text{H}_2\text{SO}_4, \text{H}_2\text{O})$ and $(\text{H}_2\text{SO}_4, 2\text{H}_2\text{O})$ fairly certainly exist in comparatively large quantity, the first being the more stable. This conclusion has been reached as a result of Jones' (*Zeitsch. physik. Chem.*, **13**, 419, 1894) investigations upon the freezing points of mixtures of sulphuric acid and water.

Before leaving the subject of molecular complexes attention

should again be drawn to the care which must be exercised in taking some abnormality in a physical property as evidence for the existence of a compound. Thus take the phenomenon of boiling. It is well known that constancy of boiling point is one of the best tests of the purity of a substance, *i.e.* evidence that we are dealing with a single substance and not a mixture. Chemists were so familiar with this test that they concluded that the constant boiling mixture of water and hydrochloric acid, which corresponds in composition to the formula $\text{HCl} + 8\text{H}_2\text{O}$, was actually a true compound. It was shown, however, by Roscoe (*Journ. Chem. Soc.* **12**, 128; *ib.* **13**, 146, 1860) that this view is not correct. Roscoe distilled aqueous solutions of HCl at different pressures, namely, at 5, 70, 80 and 150 cms. mercury. The *composition* of the mixture possessing a maximum boiling point—and therefore boiling at constant temperature when once this stage was reached—was found to differ according to the pressure at which the distillation was carried out. Thus at 76 cms. mercury the mixture possessing the maximum boiling point contained 20.24 per cent. hydrochloric acid, while the corresponding mixtures at the pressures mentioned contained 23.2, 20.4, 20.2, and 18.2 per cent. HCl respectively. Now since a chemical individual must possess the same composition under different conditions (Dalton's Law), Roscoe concluded that the constant boiling solutions of $\text{H}_2\text{O} + \text{HCl}$ were not compounds but mixtures, and that therefore the constancy of boiling point affords no proof at all in the above case that a compound $\text{HCl} + 8\text{H}_2\text{O}$ exists.

The simplest type of hydrate formation which could exist is that represented by the equation—



if A be the only solute present. Suppose that the above reaction occurs and that equilibrium is reached—as is usual in such cases—practically instantaneously. Let c be the concentration of the hydrated molecules $\text{A}(\text{H}_2\text{O})_n$ in moles per liter, c_1 the concentration of non-hydrated molecules of

the solute A, and c_2 the concentration of the water molecules.

Applying the law of mass action, the relation follows—

$$\frac{c_1 \times c_2^n}{c} = \text{a constant} = K$$

Now as long as the solution is dilute, the concentration of the water may be regarded as constant, and this term may therefore be brought over into the constant K , which now takes on a new value, K_1 , in which—

$$K_1 = \frac{c_1}{c}$$

That is to say, the concentration of the hydrated molecules bears a constant ratio to the unhydrated molecules; in other words the fraction of solute molecules hydrated, or the “degree of hydration,” is independent of the actual concentration of the solution, *i.e.* the degree of hydration is the same in a decinormal solution as it is in a centinormal one, though, of course, in the first case, the actual concentration of hydrated and unhydrated molecules is much the greater. Nernst, in his text-book, has pointed out that this conclusion respecting degree of hydration is often overlooked. It is, however, a logical consequence of the application of the law of mass action to dilute systems of this kind.

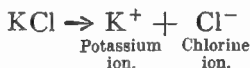
CHAPTER V

Chemical equilibrium in homogeneous systems (*continued*)—Mechanism of electrolytic conduction in solutions—The theory of electrolytic dissociation applied to aqueous solutions—Electrolytic dissociation in non-aqueous solutions.

ELECTROLYSIS. FARADAY'S LAW.

THE first fact in connection with electrolytic solutions or solutions containing one or more electrolytes is that such solutions obey Ohm's Law just as metallic conductors do. The second fact is that in solutions the transfer of electricity differs from that in metallic conductors in that the passage of the current is accompanied by a transference of matter towards the electrodes. The matter so transferred may or may not be "discharged" or set free at the electrode. Thus the electrolysis of an aqueous solution of copper sulphate, using copper electrodes, causes metallic copper to be precipitated upon the cathode (the negative electrode), an equivalent quantity of copper dissolving off the anode (the positive electrode), the positive electrode being that at which current enters the electrolysis bath, the negative electrode that at which it leaves. Using platinum electrodes in the same solution metallic copper is again precipitated upon the cathode, while at the anode oxygen gas is liberated by what is called a secondary action due to the SO_4^{--} ion having been discharged and attacking the nearest water molecule, thereby giving H_2SO_4 and liberating oxygen. Faraday introduced the idea of "*ions*," that is to say, electrically charged atoms or radicles. The solution as a whole is electrically neutral, and therefore there must be exactly as many positive ions as negative ions. The process of electrolytic dissociation of

molecules into ions may be represented in the case of potassium chloride by the equation—



or, in the more usual form, $\text{KCl} \rightarrow \text{K}' + \text{Cl}'$. These ions, Faraday considered, conduct the current, and may arrive and discharge themselves at the electrodes, the positive ion (K') travelling towards the cathode, the negative ion (Cl') travelling towards the anode. Faraday discovered two quantitative laws of electrolysis which now bear his name. They are¹:

(a) The voltametric law, which asserts that the amount of electrochemical decomposition is a precise measure of the amount of electricity conveyed.

(b) The law of electrochemical equivalence, which asserts that when a current is sent through a series of different substances, the mass of each substance liberated (or decomposed, or dissolved, or whatever happens to it) is proportional to its ordinary chemical equivalence.

These laws may be summed up in the expression—

$$w = zct$$

where w = weight of a constituent (say, copper in the CuSO_4 case) precipitated on the cathode.

z = the electrochemical equivalent of the copper, *i.e.* the quantity precipitated by unit current flowing per unit time. The electrochemical equivalent of any element is = the electrochemical equivalent of hydrogen \times chemical equivalent of the element in question.

c = current.

t = time.

It is not necessary to go into the fundamental phenomena in any further detail, since this is assumed to be familiar to the reader; we may therefore pass on to the theory which professes to account for the conducting property possessed by solutions of electrolytes, namely, the theory of electrolytic dissociation,

¹ Compare Lodge, *Brit. Ass. Report*, 1885, p. 756.

especially in regard to its bearing on osmotic phenomena and the van 't Hoff empiric factor.¹

To understand Arrhenius's argument more clearly, it is necessary to refer to the work of Kohlrausch on the subject of conductivity, and especially his law of 1876 regarding the equivalent conductivity of acids, bases, or salts at infinite dilution being made up of two separate parts, one referring to the anion, the other to the cation.

The usual method adopted for measuring the resistance (or its reciprocal, the conductivity) of an electrolytic solution consists in employing an alternating current from a small coil and using a telephone in place of a galvanometer. The object

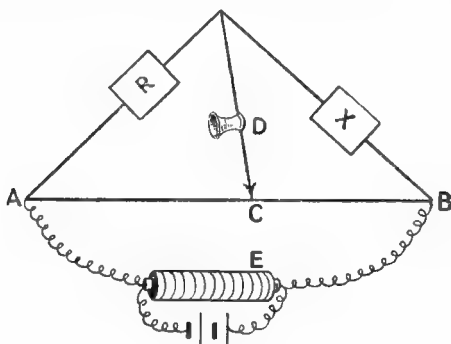


FIG. 26.

of the alternating current is to do away with polarisation effects on the electrodes, *i.e.* changes in resistance and E.M.F. due to chemical effects which accompany the discharge of acid at electrodes when a direct current is used. The principle adopted in the measurements is simply that of the Wheatstone Bridge, which is represented diagrammatically in Fig. 26.

R is the known resistance ; X the resistance of the solution ; AB is a metre wire, and the connection with the telephone D

¹ Any who wish to study from the historic standpoint the subject of electrolysis and the theories put forward, should consult the Report of the Electrolysis Committee of the British Association at their 1885 meeting.

is made by a sliding contact to the wire C, which is moved about until no sound is any longer heard in the telephone, balance between R and X having then been obtained. Frequently the arrangement is slightly different, *i.e.* telephone D and coil E are interchanged. The advantage is a practical one, in that full current is always passing through the bad (sliding) contact C. The proper balance is obtained when no current flows through the telephone, *i.e.* A *via* E to B, in the alternative arrangement to that shown in the figure. In both cases the relationship holds.

$$\frac{R}{AC} = \frac{X}{BC} \quad \text{or} \quad X = \frac{RBC}{AC}.$$

The specific conductivity ι of an electrolyte = the current which flows when the electrolyte is between electrodes 1 square cm. area, 1 cm. apart, with a P.D. of 1 volt between the electrodes.

"For¹ one and the same electrolyte this specific conductivity is naturally very much dependent on the concentration, since, as it varies, the amount of the electrolyte, contained in the 1 centimetre cube between the electrodes, must vary. The study of the specific conductivity can therefore give directly no means for finding out in what way the molecule of the substance changes its capacity for conducting electricity with varying dilution. Such a means is gained, however, from the specific conductivity, if we reduce the same by calculation to one and the same concentration—for instance to one equivalent in the centimetre cube." That is to say, if we divide the observed specific conductivity of the unit cube of liquid by the concentration of the solute in gram equivalents per c.c. we get a quantity to which the name equivalent conductivity is applied. It is the same thing to say that the equivalent conductivity is equal to the specific conductivity observed multiplied by the volume which contains one gram equivalent of the solute at the particular dilution in question. In this way we are always dealing with the conductivity due to the same *mass* of solute, and any variation in the numbers obtained must be

¹ Quotation from Abegg's *Electrolytic Dissociation Theory*.

due to some change in the *nature* of the solute individuals in the solution. Ostwald imagines the same state of affairs to be reached by picturing electrodes which remain at a fixed distance apart, 1 cm., but which with increasing dilution of the electrolyte always increase in area, so that the volume of liquid included between the electrodes always contains just one equivalent of the electrolyte. The conductivity of one equivalent (*i.e.* the "equivalent conductivity") at various dilutions is evidently a magnitude capable of giving information as regards change in the molecular condition in so far as this influences the conductivity. Since the specific conductivity is the observed conductivity of the unit cube, it is evident that as we increase the dilution we cause fewer individuals to exist between the electrodes in the cell, and though these individuals may alter somewhat in their molecular condition, *i.e.* may give rise to ions to a greater extent, their number has decreased so much that the observed conductivity also decreases. The specific conductivity therefore decreases as we increase the dilution. On the other hand, the equivalent conductivity (*i.e.* the specific conductivity reduced always to what it would be if 1 gram equivalent of the electrolyte was pushed between the electrodes, and supposing further that the molecular condition remained just as it was before the imaginary compressing process took place)—the equivalent conductivity was found by Kohlrausch to increase with increasing dilution, and in many cases reached a limit at very great dilution—such cases being solutions of the good electrolytes, *viz.* inorganic acids, bases, and salts in general. The limiting value here indicated is known as the equivalent conductivity at infinite dilution, and is represented by the symbol Λ_{∞} . Now conductivity had been long ascribed to positive and negative ions. Further the work of Hittorf has shown that these ions move under the same potential gradient with different velocities in aqueous solutions, H^+ and OH^- being by far the fastest. *Kohlrausch's relation of 1876 is known as the law of the independent migration of the ions.* He found that Λ_{∞} could be written as the sum of two effects, one due to the anions, the other to cations. He called these the mobilities of

the cation and anion respectively, and denoted them by U and V , *i.e.* $\Lambda_{\infty} = U + V$. He based this relationship on the purely additive character of the equivalent conductivities which he observed.¹

His law means that the mobility of Na^+ , for example, should have the same value whether derived from chlorides or nitrates, etc. He verified it by showing that the following held true:—

$$\{\Lambda_{\infty} \text{NaCl} - \Lambda_{\infty} \text{KCl}\} = \{\Lambda_{\infty} \text{NaNO}_3 - \Lambda_{\infty} \text{KNO}_3\}.$$

We see that the law is in agreement with this experimental fact, because—

$$\begin{aligned}\Lambda_{\infty} \text{NaCl} &= U_{\text{Na}^+} + V_{\text{Cl}^-} \\ \Lambda_{\infty} \text{KCl} &= U_{\text{K}^+} + V_{\text{Cl}^-} \\ \Lambda_{\infty} \text{NaNO}_3 &= U_{\text{Na}^+} + V_{\text{NO}_3^-} \\ \Lambda_{\infty} \text{KNO}_3 &= U_{\text{K}^+} + V_{\text{NO}_3^-}\end{aligned}$$

and therefore

$$\begin{aligned}\Lambda_{\infty} \text{NaCl} - \Lambda_{\infty} \text{KCl} &= U_{\text{Na}^+} + V_{\text{Cl}^-} - U_{\text{K}^+} - V_{\text{Cl}^-} = U_{\text{Na}^+} - U_{\text{K}^+} \\ \Lambda_{\infty} \text{NaNO}_3 - \Lambda_{\infty} \text{KNO}_3 &= U_{\text{Na}^+} + V_{\text{NO}_3^-} - U_{\text{K}^+} - V_{\text{NO}_3^-} \\ &= U_{\text{Na}^+} - U_{\text{K}^+}\end{aligned}$$

The following numerical data are taken from the extended list given by Kohlrausch (Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*). The value of Λ_{∞} was found to have reached its limit when the concentration of solute was $\frac{N}{1000}$.

Salt.	Λ_{∞}	Therefore, assuming Kohlrausch's Law to be true—
KCl . . .	129.1	$U_{\text{K}^+} - U_{\text{Na}^+} = 21.0$
NaCl . . .	108.1	
KNO ₃ . . .	125.5	,, = 20.9
NaNO ₃ . . .	104.6	
KIO ₃ . . .	97.6	,, = 20.9
NaIO ₃ . . .	76.7	
$\frac{1}{2}\text{K}_2\text{SO}_4$. . .	133.5	,, = 23.0
$\frac{1}{2}\text{Na}_2\text{SO}_4$. . .	110.5	

The constancy of $(U_{\text{K}^+} - U_{\text{Na}^+})$ is borne out by these

¹ For a discussion of the mechanical friction of the solvent see a paper by Kohlrausch, *Proc. Roy. Soc.*, **71**, 338, 1903.

results. To show, by way of illustration, how equivalent conductivity varies with concentration, finally reaching a limit, one may take Kohlrausch's values for KCl at 18° C. (data of 1885).

Concentration of salt in gram equivalents per litre.	Λ .	Difference between successive values of Λ .
1	98.2	13.7
0.1	111.9	10.6
0.01	122.5	5.1
0.001	127.6	1.9
0.0001	129.5	
$\frac{1}{\infty}$	131.2 (extrapolated)	

Now let us turn to the work of Arrhenius. His fundamental idea is that electrolytic dissociation is a function of concentration. That is to say, it is partial at ordinary concentration, and increases as we increase the dilution (*i.e.* as we decrease the concentration), becoming practically complete at infinite dilution. It will be seen how this at once gives a new significance to the rather empiric mobilities of Kohlrausch. The limiting value of the molecular or equivalent conductivity is simply reached, according to Arrhenius, when the dissociation into ions is practically complete. Not only did Arrhenius state these generalisations, but he also quantitatively made use of conductivity measurements to determine the degree of electrolytic dissociation of the solute at any given dilution. He assumed that the conductivity due to the solvent was practically nil, and ascribed all the effects to the ions of the solute. This is in agreement with experiment, in so far at least as observation goes on the conductivity of pure water, which is extremely small.

CALCULATION OF DEGREE OF DISSOCIATION BY COMBINING ARRHENIUS' THEORY WITH KOHLRAUSCH'S LAW.

By the degree of dissociation (α) is meant the fraction of each gram-molecule of solute which is decomposed into ions. Suppose that at a certain dilution we say the degree of dissociation is 0.5. This simply means that one-half of the

solute is still in the undissociated molecular state, the other half having given rise to two or more ions according to its nature, *i.e.* according to the number of atoms composing the molecule, although it must not be understood from this that the ions produced are always as numerous as the atoms from which they might be produced. Thus Na_2SO_4 gives three ions, Na^+ , Na^+ , SO_4^{--} . (Note the double charge in the ion which corresponds to the valency of the group. The solution as a whole, however, is electrically neutral.) On the other hand, H_2SO_4 , at certain concentrations, gives mainly H^+ and HSO_4^+ , while at greater dilution we get increasing quantities of SO_4^{--} . To show how α may be calculated we proceed as follows: In a given solution into which two electrodes dip—the electrodes being 1 square cm. area and 1 cm. apart—a certain e.m.f. E is maintained between them by some external means. The current which flows is given by Ohm's Law, *i.e.* $C = \frac{E}{R}$, or El_v , where l_v is

specific conductivity at this dilution, and is the reciprocal of the specific resistance. We may also view the process of current from the actual ionic effects taking place. Suppose the solution contains 1 gram-equivalent of a salt such as KCl

dissolved in v c.c.'s, then $\frac{1}{v}$ is the concentration, and supposing

the gram-equivalent of the salt to be fractionally dissociated to the extent α into two sorts of ions, *viz.* Cl^+ and K^+ , we have therefore $(1-\alpha)$ undissociated gram-equivalents, and α equivalents of anions and α equivalents of cations. Let u_c be the absolute velocity of the cation under a potential gradient of one volt/cm., then under E volt/cm. the velocity is Eu_c . Similarly let v_a be the velocity of the anion. Let F be the charge associated with each univalent gram ion, then F will be likewise the charge carried by one equivalent of any ion. The current transported per second across an imaginary plane of unit area parallel to the electrodes is made up of the sum of the parts due to cation and anion respectively. The quantity carried per second by the cation is—

$$\frac{1}{v} \alpha F E u_c$$

in one direction, while in the opposite direction the anion transports—

$$\frac{1}{v} \alpha F E v_a$$

and therefore the total current is—

$$\frac{1}{v} \alpha F E (u_c + v_a)$$

and this must be equal to $E l_v$.

Suppose now we work at a very great dilution, so that there is complete dissociation, $\alpha = 1$. Then under the same conditions of applied e.m.f. E to the same cell, the current is—

$$\frac{1}{v_\infty} F E (u_c + v_a) \text{ or } E l_\infty$$

Hence

$$\frac{E l_v}{E l_\infty} = \frac{\frac{1}{v} \alpha F E (u_c + v_a)}{\frac{1}{v_\infty} F E (u_c + v_a)}$$

$$\text{or } \alpha = \frac{l_v \times v}{l_\infty \times v_\infty}$$

but $l_v \times v =$ the equivalent conductivity at dilution $v = \Lambda_v$

$l_\infty \times v_\infty =$ „ „ „ infinite dilution $= \Lambda_\infty$

$$\therefore \alpha = \frac{\Lambda_v}{\Lambda_\infty}$$

This is Arrhenius' equation, and by its means he carried out a long series of calculations upon Kohlrausch's data for many sorts of electrolytes at various concentrations.

We are now in a position to appreciate how Arrhenius was able to explain the behaviour of those substances which had been found by van 't Hoff to be at variance with the simple osmotic law $P = RTc$, and for which he had introduced the empirical form $P = iRTc$. It will be more satisfactory to use Arrhenius' own words. For that purpose, portion of a paper of his which appeared in 1887 is here inserted, in which the subject of the osmotic pressure of electrolytes is discussed on the basis of the theory which he had put forward in 1883.

TRANSLATION OF PORTION OF A PAPER BY ARRHENIUS
 "ON THE DISSOCIATION OF SUBSTANCES DISSOLVED IN
 WATER." ¹

"In a paper presented to the Swedish Academy of Sciences on October 14, 1885, van 't Hoff demonstrated, both theoretically and by experimental results, the following extremely important generalisation and extension of Avogadro's Law:—

"'The pressure which is exerted by a gas at a given temperature, when a certain number of molecules are distributed throughout a given volume, is numerically identical with the osmotic pressure which would be exerted under the same circumstances by the majority of substances when these are dissolved in any liquid.'

"This law van 't Hoff has demonstrated in a manner which scarcely allows any doubt to exist as regards its general correctness. A certain difficulty, which still remains to be removed, exists, however, is this, that while the law holds good 'for the majority of substances,' at the same time a remarkably large number of the aqueous solutions which have been examined form exceptions in the sense that they exhibit a much greater osmotic pressure than is predicted by the above law.

"Now, when a gas exhibits anomalous behaviour of this kind with regard to Avogadro's Law, an explanation is usually found in the assumption that the gas is in a state of dissociation.

"A well-known example of this is afforded by the behaviour of Cl_2 , Br_2 , and I_2 at high temperatures, under which circumstances these bodies are considered to be split up into simple atoms.

"The same explanation naturally suggests itself in regard to the exceptions to van 't Hoff's Law. This has, however, not yet been accepted, probably on account of its novelty, and on account of the many known difficulties and objections which would be raised against such an explanation on chemical

¹ *Zeitsch. für physik. Chem.*, 1, 631, 1887.

grounds. The object of the following paper is to show that the assumption of dissociation in the case of certain substances dissolved in water, is supported to a very great degree by the conclusions which can be drawn from the electrical behaviour of these substances, and further, on closer inspection, the objections on purely chemical grounds are seen to be much diminished.

"One must assume with Clausius (*Pogg. Ann.*, 101, 347, 1857; *Wiedemann's Elektrizität*, 2, 941), in order to explain electrolytic phenomena, that a fraction of the molecules of an electrolyte is dissociated into ions, which possess the property of independent movement and migration. Since now the osmotic pressure, which a dissolved substance exerts against the walls of the containing vessel, must be considered in agreement with the modern kinetic theory, *as arising from the impacts which the smallest individual parts of this body cause by their movements against the sides of the vessel*, so one must further assume, in order to be in agreement with this, that a molecule completely dissociated in the above manner, exerts against the side of the vessel a pressure identical with what would be exerted by its ions in the free state. If one therefore could calculate, how great a fraction of the molecules of an electrolyte is dissociated into ions, one could also calculate the osmotic pressure by means of van 't Hoff's Law.

"In an earlier paper 'On the Conduction of Electricity by Electrolytes,' I have applied the term 'active' to those molecules whose ions are free to move independently of one another, and the term 'inactive' to those molecules whose ions are firmly bound together. Further, I have suggested the probability that in extremely great dilution all the inactive molecules of an electrolyte are converted into active (*Bihang der Stockholmer Akad.*, 8, No. 13, 14. Two parts, June, 1883). I shall make this assumption the groundwork of the following calculations. The ratio of the number of active molecules to the sum of *active*¹ and *inactive* molecules is denoted by the term activity coefficient. The activity coefficient of an

¹ Note that active molecules have no real existence as molecules; they represent the part which has been changed into ions.

electrolyte at infinite dilution is therefore taken to be unity. For less dilution (*i.e.* greater concentrations), it is less than unity, and according to the principles on which my work referred to is based, in the case of not too concentrated solutions (that is to say, solutions in which disturbing conditions such as changes in internal friction, etc., can be neglected) the coefficient can be put equal to the ratio of the actually observed value of the molecular [or equivalent] conductivity to its limiting value, towards which it tends on continually increasing the dilution.

"If this activity coefficient (α) is known, one can *calculate* the values of the coefficient (i) tabulated by van t' Hoff. The coefficient (i) [or in English, as it is more frequently called, 'van 't Hoff's Factor'] is the ratio of the osmotic pressure actually exerted by a body to the osmotic pressure it would have exerted had it simply consisted of inactive (non-dissociated) molecules.

"Evidently i is equal to the sum of inactive molecules plus the number of ions, the sum being divided by the number {active molecules¹ plus inactive molecules}. Thus if there are m inactive molecules and n active molecules present, and k represents the number of ions into which *one* active molecule can dissociate, then—

$$i = \frac{m + kn}{m + n}$$

For KCl, $k = 2$, namely K^+ and Cl^- ; for $BaCl_2$, $k = 3$, namely Ba^{++} , Cl^- , Cl^- ; and so on.

Since the activity coefficient α is evidently equal to $\frac{n}{m + n}$, we have

$$i = 1 + (k - 1)\alpha$$

in short, $i = \frac{\text{number of individuals actually present}}{\text{number of individuals which would be present if no dissociation had taken place}}$

¹ Note the distinction between active molecules and ions. Thus in the case of KCl, *two* ions (K^+ and Cl^-) can be produced from one active molecule. As already stated, the existence of active molecules is imaginary.

"The figures in the last column of the following table have been calculated by the aid of the above formula.

"On the other hand, one can calculate i according to van 't Hoff (as follows from the results obtained by Raoult on the freezing points of solutions), namely, by taking the lowering of freezing point of water—say t° C.—brought about by dissolving 1 gram-molecule of a given substance in 100 grams of water and dividing t° by 18.5° . The values for $i = \frac{t}{18.5}$ are given in the following table. The values given below are calculated on the assumption—as was actually fulfilled in the experiments of Raoult—that 1 gram-molecule of the substance under examination is dissolved in 10 litres of water."¹ The following table contains only a few of the data collected by Arrhenius. It is to be understood that the values of " α " are all obtained by the electrical conductivity method, *i.e.* $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$.

BASES DISSOLVED IN WATER.

Substance.	α .	$i = \frac{t}{18.5}$.	$i = 1 + (k-1)\alpha$.
Barium hydroxide	0.84	2.69	2.67
Strontium hydroxide	0.86	2.61	2.72
Sodium hydroxide	0.88	1.91	1.93
Potassium hydroxide	0.93	1.79	1.90
Ammonium hydroxide	0.01	1.00	1.03
Methylamine (methyl ammonium hydroxide)	0.03	1.09	1.03
Aniline (anilinium hydroxide)	0.00	[1]	[1]

¹ There appears at first sight to be some confusion regarding the concentration of the dissolved substances. One mole of solute in 100 grams of solvent is in many cases quite unrealisable in practice owing to solubility limitations. The solution examined is much more dilute, the lowering of freezing point actually observed being altered by simple proportion to the value it would have supposing 1 mole of solute were dissolved in 100 grams of solvent, the solute remaining in the same molecular condition as in the dilute case.

ACIDS DISSOLVED IN WATER.

Substance.	α .	$i = \frac{t}{18.5}$	$i = 1 + (k-1)\alpha$
Hydrochloric	0.90	1.98	1.90
Hydriodic	0.96	2.03	1.96
Nitric	0.92	1.94	1.92
Sulphuric	0.60	2.06	2.19
Sulphurous	0.14	1.03	1.28
Hydrogen sulphide	0.00	1.04	1.00
Boric	0.00	1.11	1.00
Acetic	0.01	1.03	1.01
Oxalic	0.25	1.25	1.49
Tartaric	0.06	1.05	1.11

SALTS DISSOLVED IN WATER.

Substance.	α .	$i = \frac{t}{18.5}$	$i = 1 + (k-1)\alpha$
Potassium chloride	0.86	1.82	1.86
Sodium chloride	0.82	1.90	1.82
Lithium chloride	0.75	1.99	1.75
Ammonium chloride	0.84	1.88	1.84
Potassium iodide	0.92	1.90	1.92
Sodium nitrate	0.82	1.82	1.82
Sodium acetate	0.79	1.73	1.79
Potassium formate	0.83	1.90	1.83
Silver nitrate	0.86	1.60	1.86
Potassium sulphate	0.67	2.11	2.33
Potassium oxalate	0.66	2.43	2.32
Barium chloride	0.77	2.63	2.54
Strontium chloride	0.75	2.76	2.50
Lead nitrate	0.54	2.02	2.08
Copper sulphate	0.35	0.97	1.35
Zinc sulphate	0.38	0.98	1.38
Magnesium chloride	0.70	2.64	2.40
Mercuric chloride	0.03	1.11	1.05
Cadmium sulphate	0.35	0.75	1.35

Arrhenius himself remarks that some of these data are not very accurate. Also, in some cases the temperature was not the same in the determinations of the last two columns. Nevertheless, there can no doubt that a very marked parallelism exists between the figures of the two columns. This shows

a posteriori that in all probability the assumptions upon which the calculation of these figures is based are in the main correct.

These assumptions—employed by Arrhenius—are:—

1. That van 't Hoff's Law is valid not only for the "majority" of substances, but for *all* substances, even for those which had been previously regarded as exceptions (electrolytes in aqueous solution).

2. That every electrolyte (in aqueous solution) consists partly of "active" molecules (in their electrolytic and chemical bearing) and partly of inactive molecules. These latter as the dilution increases become gradually transformed into active molecules, so that at infinitely great dilution only "active" molecules are present.

[Remember that active molecules have no physical existence; they represent the fraction of the molecules which have dissociated into ions.] Arrhenius concludes his paper by answering certain objections to the possibility of electrolytic dissociation.

INFLUENCE OF THE SOLVENT UPON THE MOLECULAR CONDITION OF THE SOLUTE.

Let us take as a typical group of solutes the organic acids and examine their behaviour in various solvents. In benzene solution, and at not too low concentrations, these acids are mainly in the form of double molecules; in ether, ethyl acetate, acetic acid, and similar solvents, they possess their normal molecular weight; when dissolved in water their molecular weights are slightly less than normal, *i.e.* they are slightly electrolytically dissociated. No accurate quantitative result is known in connection with the associating or dissociating power of different solvents. Nernst and Thomson have, however, independently striven to connect the dissociating power of a solvent with its *dielectric constant*, the relation being known as the Nernst-Thomson rule.¹ Water has a high dielectric constant, and is at the same time a remarkably good dissociating solvent. The introduction of a substance of large dielectric

¹ *Zeitsch. physik. Chem.*, **13**, 531, 1894.

constant would certainly tend to weaken the attraction between two oppositely charged electrified particles separated by the substance in question, since the electric force between two charges—suppose they are equal and have the value e —is given by the expression—

$$F = \frac{e^2}{K r^2}$$

where r is the distance between the charged particles, and K is the dielectric constant. Provided ions were formed at all, therefore, it will be seen that a solvent with large K would tend to cause electrolytic dissociation of the solute to be marked (Nernst even considers that the attractions between *molecules* may be considered in an analogous manner). While the Nernst-Thomson rule holds in many cases, numerous exceptions to it have been discovered, so that it must only be regarded as a qualitative generalisation. The dielectric constant of water is 81 (air = 1), and a few other liquids have also very large dielectric constants, *e.g.* liquid HCN, $K = 95$; H_2O_2 , $K = 92.8$; formamide, $K = 84$; formic acid, $K = 57$. Ordinary organic solvents have considerably smaller K values. Great dissociation is to be expected on the basis of the Nernst-Thomson rule in the case of the solvents hydrocyanic acid, formamide, and formic acid. Relatively little is known regarding this point, but it appears from the work of Walden (*Trans. Faraday Soc.*, 6, 71, 1910), that the question is not simply one of the value of the K for the solvent, but likewise depends upon the nature of the solute, *i.e.* whether it be acidic, basic, or neutral. Water is, nevertheless, usually regarded as the typical dissociating solvent.

While this is so, reference ought to be made to some recent investigations by Meldrum and Turner (*Trans. Chem. Soc.*, 97, 1805, 1910), who, instead of working with acids, bases, and salts, have investigated¹ the molecular state of a series of amides in aqueous solution in which it is shown that these bodies are actually associated or polymerised to a certain extent, instead of possessing normal molecular weights as one

¹ By the rise of boiling-point method.

would expect since they are non-electrolytes. The point has been further investigated by Peddle and Turner (*Trans. Chem. Soc.*, 99, 685, 1911) in the case of certain acids. The authors believe that the apparent association may really be due to dissociation of the solvent molecules, since liquid water is known with considerable certainty to exist partly in the form of $(\text{H}_2\text{O})_3$ and $(\text{H}_2\text{O})_2$ molecules. Previously evidence had been brought forward by Jones and Getman (*Amer. Chem. Journ.*, 32, 329, 1904), using the freezing point method to show that acetic, oxalic, and succinic acids form associated molecules in water. There is no doubt that the question of possible association of solute molecules in water has been somewhat overlooked, but so far no definite conclusion has been reached. It should be pointed out that solutes which contain OH or CN groups are very liable to association when dissolved in organic solvents, especially such solvents as benzene, diphenyl-methane, carbon disulphide, chloroform, and ethylene dibromide, *i.e.* liquids which themselves consist of *un*-polymerised molecules. It is somewhat remarkable that the *polymerisation* of the *solvent* molecules goes hand in hand with their *dissociating power* in respect of solutes dissolved in them, while normality in the *solvent* molecules entails normality or even polymerisation of the *solute* molecules.

FURTHER EVIDENCE FOR THE THEORY OF ELECTROLYTIC DISSOCIATION.

The most general conclusion to be drawn from the theory is that the properties of solutions of electrolytes—say, salts—should be capable of being represented as the *sum* of effects due to the ions, the additivity being more marked the more complete the dissociation, *i.e.* the more dilute the solution. The following illustrates certain properties of solutions from this point of view.

1. We have to deal first with the fact that such solutions conduct current at all, and further Kohlrausch's Law of independent migration of ions, and his expression for equivalent conductivity at infinite solution. We have already considered

this law, viz. $\Lambda_{\infty} = U + V$, where U and V are magnitudes characteristic of the anion and cation respectively, and we have seen that it is very satisfactorily borne out by experiment. The experimental fact that equivalent conductivity increases up to a limit as the dilution increases is the basis of the above expression.

2. *Osmotic Pressure*.—The factor i , which may be found, for example, by direct pressure measurement or by freezing-point measurement, is not connected with the specific chemical properties of each acid, base, or salt, but depends essentially on whether the substance is a binary electrolyte (one which can give rise to 2 ions, e.g. NaCl , KNO_3), ternary (one which can give rise to 3 ions, e.g. Na_2SO_4), quaternary, etc., and also on the particular concentration employed. We have already given a table of values of i . It will be seen that at comparable equivalent concentration the osmotic pressures exerted by silver nitrate and sodium chloride are practically identical, being binary electrolytes (though these substances are very different in their purely chemical effects). Also the ternary electrolytes, sodium sulphate, potassium sulphate, and strontium chloride, exhibit much the same values at comparable concentrations.

3. *Molecular Lowering of Freezing Point and Rise of Boiling Point*.—Closely connected with osmotic phenomena we may similarly group electrolytes as regards the magnitude of their molecular depression of freezing point or elevation of boiling point according as the compounds are binary, ternary, etc. There is again no specific chemical effect characteristic of each individual. The lowering of vapour pressure comes into the same category.

4. *Specific Gravity of Solutions*.—It has been found by experiment that aqueous solutions can be represented fairly closely by an expression such as—

$$\rho = \rho_0 + \alpha c + \alpha_1 c^2$$

where ρ = density of the solution ;

ρ_0 = „ „ solvent ;

c = concentration of solute—say in gram equivalents/liter ;

α and α_1 are constants determinable by experiment.

For ordinary purposes it has also been found that this simple expression gives sufficiently close values, viz.—

$$\rho = \rho_0 + \alpha c$$

Suppose now we have a solution containing two substances, A and B. For solutions which contain A as solute alone the expression holds—

$$\rho = \rho_0 + \alpha c_1$$

and for the solution of B alone—

$$\rho = \rho_0 + \beta c_2$$

then on mixing the two solutes so that the solution is c_1 normal with respect to A, and c_2 normal with respect to B, we get—

$$\rho = \rho_0 + \alpha c_1 + \beta c_2$$

Now if we assume electrolytic dissociation to be true, and take a very dilute solution of a salt which is presumably practically completely dissociated, *e.g.* sodium chloride into sodium ions and chlorine ions, we may look upon these ions as corresponding to the two substances A and B, always present, however, in equivalent concentration. Now let us suppose we had four solutions, viz. a solution of sodium chloride, possessing a density value ρ_{NaCl} ; sodium bromide, density ρ_{NaBr} ; ammonium chloride, $\rho_{\text{NH}_4\text{Cl}}$; ammonium bromide, $\rho_{\text{NH}_4\text{Br}}$. Further, let α be the coefficient (in the density expression) for Na^+ ion; and similarly let β refer to Cl^- ion; γ to Br^- ion; δ to NH_4^+ ion.

Then if we take as a special case 0.1 normal solution of these four salts, we have the relations ($\rho_0 = 1$)—

$$\rho_{\text{NaCl}} = 1 + 0.1 (\alpha + \beta)$$

$$\rho_{\text{NaBr}} = 1 + 0.1 (\alpha + \gamma)$$

$$\rho_{\text{NH}_4\text{Cl}} = 1 + 0.1 (\delta + \beta)$$

$$\rho_{\text{NH}_4\text{Br}} = 1 + 0.1 (\delta + \gamma)$$

and consequently—

$$\rho_{\text{NaCl}} - \rho_{\text{NaBr}} = \rho_{\text{NH}_4\text{Cl}} - \rho_{\text{NH}_4\text{Br}}$$

that is, provided we are dealing with an additive property—the above equations being a typical way of expressing such a state of things. Experiment (*e.g.* Valson, *C. R.*, 73, 441,

1871; 77, 806, 1873) has shown the above expression to be in accordance with fact, and hence we have support for the dissociation theory, since it likewise requires the property in great dilution to be an additive one.

5. *Optical Refractivity of Solutions*.—The refractive index of the solvent—water—is first determined. It is then found possible by a suitable choice of moduli or coefficients which are supposed to be characteristic of the ions, to calculate what the refraction index would be for a solution of any given concentration. Experiment goes to show that the property is an additive one, the agreement between calculated values and those experimentally obtained being moderately good.

6. *Optical Activity or Natural Rotatory Power of Solutions*.—Some organic compounds are capable of rotating the plane of polarisation of light passed through them. If therefore a series of salts containing an optically active anion and inactive cations be examined, then equivalent quantities of all the salts should have equal rotatory power, if the dilution is sufficiently great to allow dissociation to be practically complete. This has been confirmed, for example, in the case of the salts of quinic acid, the anion of which salts is active. A series of $\frac{N}{7}$ solutions ¹ give the following molecular rotations:—

Potassium quinate, 48·8	Barium quinate, 46·6
Sodium „ 48·9	Strontium „ 48·7
Ammonium „ 47·9	Magnesium „ 47·8

It should be noted particularly that the molecular rotation of the active *free acid* itself—not the anion—is 43·4, a number which differs from the constant value obtained for the salts.

Quite similar results are obtained with the camphorates (*i.e.* Na, K, Li, Ba, Ca, Mg, NH₄ camphorates). It has been observed that as we increase the dilution, the molecular rotatory power of all these salts tends to the same constant limit, namely, 39°. This relation is known as Oudemann's Law. The value found for *free* camphoric acid in dilute solution is

¹ A better test of the theory would have been afforded had these solutions been much more dilute.

a quite different matter, however, namely, 93° . It is, therefore, impossible to try and explain the convergence of the values for the salts as being due to the progressive dissociation into acid and base (as used to be believed), for if so one would expect to reach the value 93° , since the base is quite inactive. The fact that we reach quite a different value, viz. 39° , is extremely strong evidence in favour of the electrolytic dissociation theory, for according to this, dissociation does *not* take place into acid and base, but into electrically charged cation and anion. The value 39° , therefore, is due to the *ion* of camphoric acid, whilst 93° is due to the molecule of camphoric acid, since camphoric acid is scarcely dissociated at all. The theory thus affords a very satisfactory explanation of Oudemann's Law.

7. *Absorption Spectra of Solutions.*—When one passes a beam of white light through a prism so as to spread it out into a spectrum containing all the colours continuously from red to violet, it has been found that by interposing a vessel containing a solution, it very frequently happens that certain of the colours are now absent, *i.e.* have been absorbed by the solution. This naturally must occur with coloured solutions, since the colour is due to absorption, though it should also be remembered that what we call colourless solutions may also show absorption for different wave-lengths other than those contained in the relatively short range which the eye can detect, and which we call the visible spectrum. At present, however, we are considering visibly coloured solutions. A very striking confirmation of the electrolytic dissociation theory was afforded by the work of Ostwald (*Zeitsch. physik. Chem.*, 9, 579, 1892) on the permanganates in aqueous solution. By photographing the spectrum thus produced, on the same plate, spectral images of different solutions, which contained the same coloured anion in equivalent quantities with various cations. A number of absorption bands were produced by the interposition of the solutes, and the important point is that when the solutions were dilute 0.002N, the bands for each salt (*e.g.* sodium permanganate, potassium permanganate, ammonium permanganate, etc.) fell at exactly the same place. The spectrum was

independent of the nature of the cation, except in a few cases where deviations occurred, and could be attributed to disturbing secondary effects. The identity of the spectra could be expected from the theory of free ions.

It should be pointed out, however, that Ostwald's conclusion in this connection has been recently criticised by Merton,¹ who photographed the absorption spectra of various permanganates in various solvents. He found that the position of bands in any single solvent is the same for permanganates of potassium, sodium, calcium, barium, zinc, etc., and he therefore suggests—since some of the solvents employed could only possess very slight ionising power—that the absorption is due to the MnO_4 group, and is not much influenced by ionisation. Chemical reaction between the solvents and the solutes prevented determinations of concentration. Naturally, if Merton's view is correct as regards the unimportance of dissociation, it is clear that Ostwald's results cannot be urged as positive evidence in favour of the electrolytic dissociation theory. [For a very complete discussion of optical properties from the chemical standpoint, the reader is referred to E. C. C. Baly's "Spectroscopy" (Sir William Ramsay's series of Text-books).]

In connection with the phenomena of colour it should be mentioned that the application of indicators in acidimetry and alkalimetry is based upon the colour changes involved (directly or more probably indirectly) in passing from the undissociated to the dissociated state, or *vice versa*, or rather the theory of electrolytic dissociation has been shown to give a rational explanation of the reactions referred to.

8. *Specific Catalytic Effects attributed to Ions.*—It has been observed that many reactions in solution take place very slowly if the substance or substances are alone present in the solvent, while the rate of reaction is increased by the addition of certain substances which apparently take no definite stoichiometric part, *i.e.* they do not appear in the ordinary form of writing the reaction equation. This action, which apparently is merely due to the presence of the substance, is called

¹ *Trans. Chem. Soc.*, **99**, 637, 1911.

catalysis, the accelerating substance being called a catalyser or catalyst. There are two sorts of catalysis—homogeneous and heterogeneous. We are only dealing with homogeneous at present, *i.e.* the catalysis due to some substance which itself dissolves in the solution in which the reaction is taking place. The typical example of a reaction which can be catalysed is the conversion of cane sugar into dextrose and laevulose in aqueous solution. At ordinary temperatures this takes place very slowly, the reaction equation being—



When, however, we add acids such as HCl, HNO₃, H₂SO₄, the reaction goes much faster and further, the speed depends on the concentration of the catalyst. For dilute solutions of the acid the reaction velocity is practically proportional to the equivalent conductivity of the acid (Ostwald, *J. prakt. Chem.*, 28, 449, 1883; 29, 385, 1884; 30, 93, 1884). Now the only thing these and other acids have in common is the H atom, which on the electrolytic dissociation theory becomes H⁺ ion, and the catalysis is considered as due to this. Further, on the theory the concentration of the H⁺ ion is the ratio $\frac{\Lambda_v}{\Lambda_\infty}$, and since Λ_∞ , as shown by Kohlrausch, has very much the same value for all acids, it would follow that the relative catalytic effect of different acids should be proportional to the equivalent conductivity.

Ostwald obtained the numbers given in the following table for Λ and k_1 (the velocity of inversion of the sugar). [We shall study velocity of reactions later on by themselves, and see then the exact meaning of k_1 .] The equivalent conductivity of HCl (in 1 normal solution) is set equal to 100 (though this is not its value when expressed in the usual units); and the velocity of inversion, caused by the same acid (in 0.5 N solution) is also set equal to 100.

Acid.	Λ .	k_1	k_2
HCl	100	100	100
HNO ₃	100	100	92
H ₂ SO ₄	59.5	54	55
Trichloracetic	—	75	68
Dichloracetic	33.0	27.1	23
Monochloracetic	6.41	4.84	4.3
Acetic	0.67	0.4	0.34

The values denoted by k_2 are the velocities of saponification of an ester in presence of 0.67 normal solutions of the acids mentioned. There is a marked parallelism in the values for the velocities and equivalent conductivities. More accurate determinations were carried out later by Arrhenius (*Zeitsch. physik. Chem.*, **4**, 244, 1889), and Palmaer (*Zeitsch. physik. Chem.*, **22**, 492, 1894). This work showed that at a high dilution the velocity of inversion and the fraction of the acid dissociated are directly proportional. The above effects are considered as due to the H⁺ ions. We likewise have examples of catalytic effects due to other ions, *e.g.* OH⁻ ions.

9. *Mixtures of Salts in Solution.*—A striking fact in connection with the chemical properties of salts in solution is that the acidic and basic portions generally exhibit exactly the same reactions, independent of the particular salt of which they originally formed the constituents. Thus, *all* soluble barium salts give with all soluble sulphates exactly the same reaction, namely, the formation of barium sulphate. Similarly, AgNO₃ will precipitate AgCl from any soluble chloride, KCl, NaCl, CuCl₂, BaCl₂, etc. This is quite characteristic of inorganic salts in aqueous solution, so much so that it has been found possible to draw up a scheme of analysis whereby the constituents of a solution may be detected and recognised simply by applying this conception of the specific effect of each constituent. It will be obvious how simply this is explained on the assumption of free ions. Our systems of qualitative and quantitative analyses are based essentially on reactions of ions. There are cases, however, which appear to contradict these simple statements. Take for example a silver salt and add KCN

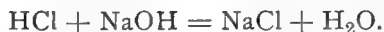
solution. At first a white precipitate is formed which redissolves on adding excess of KCN, and this solution no longer gives the ordinary reaction for silver (ion), say, on adding KCl. It has long been assumed that a complex was formed, and by introducing this idea into the ionic theory we arrive at the concept of a complex ion. Migration experiments, *i.e.* measurements of the motion of ions in an electric field, have conclusively shown that such ionic complexes do actually exist. In the particular case cited it has been shown that the *direction* in which the silver has moved (by ultimately analysing the liquid at different places) is toward the anode (the + pole). The silver must therefore be present as a complex anion instead of in its ordinary state as Ag^+ cation. As a matter of fact, experience has shown that in excess KCN solution the silver is present as the anion $(\text{AgCN})'$, the cation being K^+ . This explains the absence of the ordinary reactions due to Ag^+ , for this no longer exists in appreciable amount in the solution. Similar instances occur when AgCl is dissolved in NH_3 ; when NH_3 is added to solutions of copper salts; and when mercuric iodide HgI_2 is dissolved in KI solution. The idea of simple ions and complex ions has been found sufficient to afford an explanation for all the reactions of aqueous solutions. In the case of organic bodies in solution, however, we generally find these to be non-electrolytes. We therefore assume that no ions are present; and hence any system of analysis of organic substances in solution comparable with our systems of inorganic analysis is impossible.

A question which has frequently arisen is—What happens when two salts, say K_2CO_3 and Na_2SO_4 , are mixed together in aqueous solution? According to the electrolytic dissociation theory, these salts would be very largely split up into their ions. That is to say, the solution would contain on the simplest assumptions, Na^+ , K^+ , CO_3'' , SO_4'' , and it is clear that it is quite impossible to tell to what salt these ions originally belonged, for in the solution they have become independent of the constituent originally combined with them. The dissociation theory is thus in good agreement with these

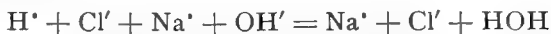
observations. A further point to notice is that the dissociation takes place with immeasurably rapid velocity, *i.e.* it is instantaneous to all intents and purposes.

10. *Physiological Action of the Ions.*—This has been developed to a very great extent recently, notably by Arrhenius in his *Immuno Chemistry*. We shall only consider a single illustration—the poisonous property. The results of investigation showed that all potassium salts have nearly the same poisonous effect in solutions of equal concentration. This, of course, does not hold when the anion is likewise poisonous, as in the case of KCN. Kahlenberg (*Journal Physical Chemistry*, 4, 553, 1900), and Loeb (*Pflüger's Archiv.*, 69, 1897; 71, 457, 1898), as well as Paul and Krönig (*Zeitsch. physik. Chem.*, 21, 414, 1897), have investigated the action of salts on bacteria and spores, and the results are in general what would be expected on the basis of the dissociation theory.

11. *Heat of Neutralisation of Acids and Bases.*—The reaction in a typical case of neutralisation is usually represented thus—



According to the dissociation theory (assuming it to be true), when we add acid to the base we have in solution the following ionic reaction:—



It will be noted that we have not written $\text{H}^+ + \text{OH}'$ in the last term. We know from conductivity experiments that water is almost a non-conductor, that is to say, the quantity of H^+ and OH' present is extremely small.

When neutralisation occurs, therefore, practically all the H^+ and OH' unite to form undissociated water. But it will be noticed in the above ionic reaction that Na^+ and Cl' appear in exactly the same condition on both sides of the equation. Eliminating these common terms, we get as the nucleus of the total reaction—



The heat of neutralisation of a practically completely dissociated acid with a similarly dissociated base is simply due to

the formation of water from its ions. For all strong acids and bases the heat should, therefore, be the same for the same amount of water formed. This has been found to be the case, viz. approximately 137 centuple calories (1 centuple calorie = 100 gram-calories) per gram-molecule of water produced. Dilute solutions of the following acids were neutralised with caustic soda also in dilute solution.

		Heat of neutralisation.	
HCl	137	centuple calories, K
HBr	137	" "
HI	137	" "
HClO ₃	138	" "
HBrO ₃	138	" "
HIO ₃	138	" "
HNO ₃	137	" "

A similar table for the heat of neutralisation of strong bases by a strong acid (HCl) is given :—

		Heat of neutralisation.	
Lithium hydroxide	138	centuple calories, K
Na	"	137	" "
K	"	137	" "
Tl	"	138	" "
Ba	"	139	" "
Sr	"	138	" "
Ca	"	139	" "
Tetramethylammonium hydroxide	137	" "

When, however, we work with weaker acids or bases, *i.e.* those which are not completely (or nearly completely) dissociated at the dilutions employed, the results are different. It seems reasonable to ascribe this to the (positive or negative) heat of *dissociation* of the weak acid or base. Using caustic soda as base (practically completely dissociated) and neutralising with weak acids, the following results were obtained :—

Metaphosphoric	143 K
Hydrofluoric	163 K
Acetic	134 K

while for weak bases neutralised by the strong acid HCl, the following figures have been obtained:—

Ammonia (ammonium hydroxide)	122 K
Methylammonium hydroxide . .	131 K
Diethylammonium hydroxide . .	118 K
Triethylammonium hydroxide . .	87 K

Note that some of these numbers are above 137K, some below. As regards the reaction here occurring, the weak acid or base must dissociate more and more in order to keep itself in equilibrium with its ions, one of which is disappearing to give H₂O. We might look upon the process as first of all involving a dissociation of the weak acid or base, and this means a heat effect. Also it is important to remember that salts containing a weak acid or base, or both, suffer more or less extensive hydrolytic decomposition owing to action of the water (the solvent), *e.g.* sodium acetate in water undergoes a partial decomposition according to the equation—



Thus we find a little free acetic acid and free alkali in the solution. Owing to the dissociation of acetic acid being extremely small, and that of caustic soda being practically complete, the result is that the solution reacts alkaline. Alkalinity or acidity is very characteristic of hydrolysis, but we shall not consider the point at this stage. The important thing for the present to note is that we can have acetic acid and alkali coexisting (to a small extent) without further formation of salt, *i.e.* the neutralisation process which occurs when we add NaOH to acetic acid does not go quite completely, and hence, owing to this cause, there is not the normal heat evolution of 137K per equivalent but something less than this. In the case of weak bases or acids, therefore, the normal heat values is not observed owing generally to the two simultaneous secondary effects—*viz.* the progressive dissociation of the weak component, “heat of dissociation,” and the incompleteness of neutralisation. The theory of free ions affords the best explanation we have yet got for both the normal values

and the abnormal. It may be mentioned that from electromotive force measurements the heat evolved in H_2O formation can be even calculated and comes out about 137 K.

12. *Evidence from the Measurements of Electromotive Force of Cells.*—The great advances which, since 1888, have been made in the study of the electromotive force, and especially the conception of a “reversible electrode,” could not have been rendered possible without the dissociation theory.¹ The evidence of these phenomena must, however, be postponed until we are in a position to consider the matter from the standpoint of thermodynamics.

It has been claimed more than once that the abnormal osmotic pressures exhibited by strong electrolytes can be explained by the hypothesis of a hydrolytic decomposition into acid and base, for instance—



This assumption is shown to be quite inadequate, in the first place, by the fact that the acid and base which in their turn *cannot* undergo a hydrolytic change of the above nature also show, like the salt, abnormal osmotic pressures; secondly, if the above were true, the heat of neutralisation should not be a constant quantity for strong acids and bases, nor should it come out to be (as it is) identical with the heat of formation of water; thirdly, results such as those of Oudemann on the optical rotary power of salt solutions (say, of camphoric acid), at great dilution, in which the limiting value for the rotation differed quite markedly from that of the free acid, contradict any such hypothesis. The conception of free ions, however, affords, as already shown, very satisfactory explanation of all these phenomena.

Having now reasonably established the *existence* of ions, we may go on to study some of the consequences of the electrolytic dissociation theory. Let us first of all consider the motion of the ions in an electric field.

¹ Especially results such as those obtained from gravity and centrifugal cells. Cf. Tolman, *Proc. Amer. Acad.*, Sept., 1910.

SOME CONSEQUENCES OF THE ELECTROLYTIC DISSOCIATION THEORY. THE "MOBILITY" OF THE IONS AND THEIR ABSOLUTE VELOCITIES UNDER A GIVEN POTENTIAL GRADIENT.

We have already discussed (p. 227) the generalisation known as Kohlrausch's Law, namely, that the equivalent conductivity, say, of a binary electrolyte such as KCl, at infinite dilution (*i.e.* at a dilution so great that dissociation is complete) may be represented as the sum of two independent quantities called the mobility of the cation and anion respectively—

$$\Lambda_{\infty} = U_c + V_a$$

We have likewise shown that (p. 231)—

$$\Lambda_{\infty} = F(u_c + v_a)$$

where $F = \text{one Faraday} = 96540 \text{ coulombs.}$

u_c and $v_a = \text{absolute velocity in cms. per second of each ion}$
under a potential gradient of 1 volt per centimetre.

Hence it follows that—

$$\begin{array}{l} U_c = F u_c \\ V_a = F v_a \end{array} \quad \text{and} \quad \frac{U_c}{V_a} = \frac{u_c}{v_a}$$

If we could measure U_c or V_a , we could calculate u_c or v_a , and *vice versa*; and having got one of these quantities, we could apply Kohlrausch's Law to get the corresponding values of any other ion.

We shall first of all deal with the work of Hittorf who measured the *ratio* $\frac{U_c}{V_a}$ (or $\frac{u_c}{v_a}$) for several cases. If we increase the fraction $\frac{U_c}{V_a}$ by unity, we get $\frac{U_c + V_a}{V_a}$, and to the reciprocal of this expression, viz. $\frac{V_a}{U_c + V_a}$ (or $\frac{v_a}{u_c + v_a}$), Hittorf gave the name "*Transport number of the anion.*" To the corresponding expression, $\frac{U_c}{U_c + V_a}$ (or $\frac{u_c}{u_c + v_a}$), he gave the name

"*Transport number of the cation.*" His method of measurement of transport numbers consisted essentially in allowing a known quantity of electricity to flow for a time through the solution in question. He then analysed the liquid in the region of the anode and cathode, and determined the change in concentration of the corresponding ions, which had taken place owing to the wandering of the ions during the electrolysis. If the transport number for, say, the cation of any given salt were to come out unity, it would mean that the entire current had been carried by this ion. This is quite an imaginary case, since it would require one of the ions to move infinitely slowly compared with the other under the same conditions as regards electric field. The transport number 0.5, which is what one finds nearly reached in many cases, would mean that half the current is carried by the cations, half by the anions. The most exact measurements of transport numbers yet made refer to KCl, which give 0.497 for the K^+ cation at $18^\circ C$. We may therefore regard the transport number, say, of the cation, either as the ratio of its velocity to the sum of the absolute velocities of anion and cation, or as the ratio of the mobility of the cation to the sum of the mobilities of cation and anion, or as the fraction of the total current carried by the cation, for evidently the greater the mobility or velocity, the greater the number of coulombs transferred in a given time, and if we introduce a proportionality factor to indicate the connection between the two quantities, it will be seen that the factor vanishes in the ratio $\frac{U_c}{U_c + V_a}$, the sum $U_c + V_a$ being proportional to total current, and U_c proportional to the fraction carried by the cation.

A very simple type of apparatus for measuring transport numbers is shown in Fig. 27. A is an electrode of silver, C an electrode of platinum or copper. The vessel is supposed completely filled with silver nitrate solution, and current is passed through the cell from left to right. The Ag^+ ion moves from left to right towards the cathode C. The NO_3^- ions move in the opposite direction. Q units of electricity pass through the cell, this current being measured by means of a

copper voltameter placed in circuit. Silver dissolves off A corresponding to the quantity of electricity Q . If the Ag^+ ions did not move at all, the solution in the long limb would have increased in Ag^+ ion concentration by an amount electro-

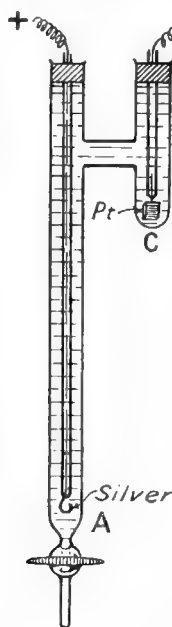


FIG. 27. — Apparatus for measuring the Transport Number of the Silver ion in Silver Nitrate solution.

chemically equivalent to Q . But since Ag^+ ion *does* move, it will be found by analysis of the contents of the anode compartment that the increase in the mass of silver (in the ionic form, of course) is not as great as that which corresponds to Q . The difference between the mass of silver which should have been finally present in the compartment had no movement of the Ag^+ ion taken place, and the mass actually present represents the quantity transported. This mass of silver divided by the mass of silver which corresponds to Q , is the transport number of the silver ion.¹ This quantity subtracted from unity gives at once the transport number for the anion. At ordinary temperatures the transport number of Ag^+ is not very different from that of NO_3^- , the latter being the greater of the two.

We may now advance a step further by combining the transport number

$\frac{U_c}{U_c + V_a}$ with the equivalent conductivity

at infinite dilution, taking Kohlrausch's Law into consideration. Thus, in the particular case of potassium chloride, experiment shows that at 18°C . the transport number of the cation, viz.—

$$\frac{U_c}{U_c + V_a} = 0.497$$

¹ For a concrete case showing the details of calculation, the reader should consult a textbook of practical physical chemistry, *e.g.* Findlay's *Practical Physical Chemistry*.

Also $\Lambda_{\infty} = 130.1$ (the units being the reciprocal ohm and concentration in equivalents per c.c.)
 $= U_c + V_a$

Hence $\frac{U_c}{130.1} = 0.497$

and hence $U_c = 64.67$ under a gradient of 1 volt per cm. By subtraction one finds $V_a = 65.44$ under the same gradient.

Further, these mobility terms are connected with the absolute velocity of the ions (under unit potential gradient) by the relation $U = Fu_c$; $V_a = Fv_a$. Therefore, in the above case, since F is always 96,540 coulombs, it follows that the absolute velocity u_c of the cation under a potential gradient of 1 volt per cm. is 6.7×10^{-4} cms. per second, the corresponding value for the anion v_a being 6.78×10^{-4} cms. per sec. It will be observed that the ions under unit gradient move very slowly. In the following table are given the values of the mobility and absolute velocity of a number of ions in aqueous solution at 18° C., under a potential gradient of 1 volt per cm. It will be observed that H^+ ion is the most rapidly moving ion, OH^- coming next at about one-half the value of the H^+ ion.

Ion.	Temperature 18° C. Absolute velocity in cms. per second.	Mobility.
H^+	32.50×10^{-4}	318
K^+	6.70 "	64.67
Na^+	4.51 "	43.55
Li^+	3.47 "	33.44
Ag^+	5.70 "	54.02
OH^-	17.80 "	174
Cl^-	6.78 "	65.44
NO_3^-	6.40 "	61.78
CH_3COO^- . .	3.20 "	35

NOTE.—At 25° C. the most probable value for the mobility of H^+ ion in very dilute aqueous solution is 347.2 (cf. Kendall, *Trans. Chem. Soc.*, 101, 1283, 1912).

One can see, therefore, that the equivalent conductivity at

infinite dilution of *acids* must be greater than bases, and these greater again than salts under the same condition. Of course this is arguing backwards, for it is from the value of Λ_{∞} that the mobility and velocity values are obtained as a rule. Besides this indirect method, however, we are indebted to Lodge for the first *direct* determination of the absolute velocity of H^+ ion (*Brit. Assoc. Rep.*, 1886, p. 389). The apparatus is represented diagrammatically in Fig. 28.

The horizontal tube contains set gelatine impregnated



FIG. 28.

with a little phenolphthalein and sodium chloride, to which has been added a trace of $NaOH$, just sufficient to colour the phenolphthalein red. When current is passed, H^+ ions from the acid move in a certain direction, decolorising the jelly tube as they move, and by reading the shift of the colour boundary at certain time intervals, the velocity of the H^+ ion is got directly for the particular potential applied between the electrodes. One can easily calculate from this the velocity under 1 volt per cm. Lodge's first experiment gave the result 29×10^{-4} cms. per second under 1 volt per cm.; later experiments gave 26×10^{-4} , and 24×10^{-4} respectively. It will be seen that these—especially the first—are in fairly good agreement with Kohlrausch's indirectly-found value 32×10^{-4} . Lodge also employed the gelatine tube method for other ions. He found, for example, that SO_4 travels at about one-third the speed of H^+ ion.

At a later date Whetham¹ introduced a modification of Lodge's method which is applicable to *coloured* ions, say, cupric ion Cu^{++} in copper sulphate solution. Above the layer of copper sulphate solution there was carefully poured a colourless solution of a salt with the same anion, having the same

¹ *Phil. Trans.*, 337, A, 1893; 507, A, 1895.

specific conductivity as the copper salt, this being necessary to keep the potential gradient the same along the tube. On applying the potential in the proper direction, the Cu^{++} ions moved into the colourless solution so that the position of the surface of demarcation moved, and the extent of this movement in a given time could be measured. This "moving boundary method" was further extended notably by Steele¹ to colourless solutions, the movement of the boundary being measured by the change in refractive index which occurs as the boundary passes through the field of vision of a refractometer. A source of error in this type of measurement due to the movement of the solvent itself along the walls of the tube, a process known as "cataphoresis" or "electrical endosmose," was pointed out by Abegg and Gaus² who also showed how this could be corrected for. This work was extended by Dennison,³ whose paper should be consulted as well as that of Lash Miller.⁴

EXAMPLES OF THE *EXTENT* OF ELECTROLYTIC DISSOCIATION.

(A) *In the case of strong electrolytes* (good conductors of electricity).

Taking sodium chloride dissolved in water, Kohlrausch obtained the following values for the equivalent conductivity at 18° C. The dilution v denotes the volume in liters which contains one gram-equivalent of the solute; α denotes the fraction of an equivalent or mole of NaCl which suffers dissociation.

¹ *Phil. Trans.*, 198A, 105, 1902; *Zeitsch. physik. Chem.*, 40, 689, 1902.

² *Zeitsch. physik. Chem.*, 40, 737, 1902.

³ *Ibid.*, 44, 575, 1903.

⁴ *Zeitsch. physik. Chem.*, 69, 436, 1909.

γ_+	Λ_+	α_+	$100 \times \alpha_+$, i.e. the number of moles dissociated per 100 moles in solution.
1	69.5	0.675	67.5
2	75.7	0.736	73.6
10	86.5	0.841	84.1
20	89.7	0.872	87.2
100	96.2	0.935	93.5
500	99.8	0.970	97.0
1,000	100.8	0.980	98.0
5,000	101.8	0.989	98.9
10,000	102.9	$\left\{ \begin{array}{l} \text{practically unity,} \\ \text{i.e. complete dis-} \\ \text{sociation.} \end{array} \right\}$	100
50,000	102.8		
100,000	102.4		

Similarly, for NH_4Cl , at the same temperature :—

γ_+	Λ_+	$\alpha =$ dissociated fraction of one mole of solute.
1	90.7	0.750
2	94.8	0.784
10	103.5	0.856
20	107.8	0.892
100	114.2	0.945
500	118.0	0.976
1,000	119.0	0.985
5,000	120.4	practically unity
10,000	120.9	
50,000	120.9	

SILVER NITRATE, AT 25° C.

γ_+	Λ_+	α_+
16	102.25	0.828
32	108.00	0.874
64	111.02	0.899
128	114.34	0.926
256	116.87	0.947
512	118.75	0.962
	$\Lambda_\infty = 123.45$	

HYDROCHLORIC ACID, AT 25° C.

$v.$	$\Delta.$	$\alpha.$
2	331	0.876
4	343	0.907
8	355	0.939
16	362	0.955
256	378	1.000 approx.
	$\Delta_{\infty} = 378$	

POTASSIUM SULPHATE, AT 18° C.

$v.$	$\mu.$	$\alpha.$
2	134.4	0.527
4	147.2	0.577
20	179.4	0.703
40	191.8	0.752
200	219.6	0.861
1,000	236.2	0.926
10,000	248.2	0.973
20,000	255.0	1.000 approx.
	$\mu_{\infty} = 255$	

NOTE.—The symbol μ in the above case and the following case denotes molecular conductivity, which is double the equivalent conductivity for such salts.

BARIUM CHLORIDE, AT 18° C.

$v.$	$\mu.$	$\alpha.$
20	172.2	0.753
40	180.8	0.791
200	201.2	0.880
1,000	214.8	0.939
2,000	218.4	0.955
10,000	223.6	0.978
100,000	228.8	1.000 approx.
	$\mu_{\infty} = 228.6$	

It will be noticed that salts, acids, etc., containing monovalent atoms tend to give rise to the greatest dissociation into

ions; divalent solutes, *i.e.* electrolytes containing a divalent radicle, dissociate less, and trivalent still less. It is convenient to remember that salts of monovalent ions, *e.g.* the alkali salts, when at a concentration of $\frac{N}{10}$, are dissociated to approximately 85 per cent., while divalent salts are not higher than 70 per cent. and may be much less (*e.g.* CuSO_4 $\frac{N}{10}$ solution dissociation is only about 30 per cent.). Trivalent salts are about the region of 50 per cent. dissociation or less in $\frac{N}{10}$ solution (Noyes' Rule).¹ It will be seen, however, when we compare these with the dissociation of some typical weak electrolytes in the next table, that the two sets are not even of the same order of magnitude. The examples given are typical, but it must be remembered that there is no sharp dividing line between strong and weak electrolytes, there being quite a continuous series of substances from one group to the other.

(B) *The Extent of Dissociation in the case of Weak Electrolytes* (those which conduct current badly).

A typical example is that of *Acetic Acid* in water. The following data hold for 25° C. :—

$v.$	$\Lambda.$	$\alpha.$	100 $\alpha.$
8	4.34	0.01193	1.193
16	6.10	0.01673	1.673
32	8.65	0.02380	2.380
64	12.09	0.0333	3.33
128	16.99	0.0468	4.68
256	23.82	0.0656	6.56
512	32.20	0.0914	9.14
1024	46.00	0.1266	12.66
	$\Lambda_{\infty} = 364$		

It will be observed that at a dilution $\frac{N}{1000}$ the fraction

¹ Recent investigations by G. N. Lewis seem to point to smaller values of α than those quoted (*Journ. Amer. Chem. Soc.*, **34**, 1631, 1912).

dissociated is only about 12 per cent., while in the case of HCl it is 100 per cent.

An interesting point is how the value 364 for Λ_{∞} for acetic acid is arrived at. It is evident that throughout the range of the dilutions employed, even up to 1024, the Λ shows no sign of reaching a limiting value as it did in the case of the strong electrolytes mentioned. The true value for Λ when dissociation is complete cannot as a matter of fact be obtained directly for weak electrolytes, because at the dilution which would have to be employed—it would be several millions of liters—the observed conductivity would be practically identical with the value for the water, for even the best conductivity water contains, under ordinary conditions, slight traces of impurities, *e.g.* CO_2 , which give to it a certain amount of conductivity quite sufficient to mask any effect due to the acetic acid were the solution so dilute as to allow of the acetic acid being completely dissociated. The method of determining Λ_{∞} is based on Kohlrausch's Law of the independence of the mobility values of the ions. It is a remarkable fact that even although an acid—as acetic acid—may be extremely weak, its potassium or sodium salt is dissociated to practically the same extent in water as an inorganic salt like NaCl. We can therefore easily observe the equivalent conductivity of sodium acetate when the dissociation is complete, and knowing previously the mobility of the sodium ion we get by subtraction the mobility of the acetanion $\text{CH}_3\text{COO}'$. Now if we add to this the already known mobility of H' , we get as a result the Λ_{∞} for acetic acid. This is how the number 364 was obtained above. Since H' itself contributes the value 318, it is evident that it has the predominating influence, so that practically all acids have approximately the same value for Λ_{∞} .

As a typical base which is a weak electrolyte one may instance ammonia. The following values hold for 25° C. :—

c .	Λ .	α .
8	3.20	0.0135
16	4.45	0.0188
32	6.28	0.0265
64	8.90	0.0376
128	12.63	0.0533
256	17.88	0.0754
	$\Lambda_{\infty} = 237$	

The base here considered is NH_4OH , which gives rise to NH_4^+ and OH' ions to the extent indicated by α .

An $\frac{\text{N}}{10}$ solution of NH_3 is therefore about 1.5 per cent. dissociated, while NH_4Cl is 85 per cent. dissociated—a very striking example of the phenomenon alluded to above, viz. that the *salt* formed from a weak acid or weak base is itself a strong electrolyte. This is even true in the case of *ammonium acetate* where *both* acid *and* base are weak.

THE FUNDAMENTAL EQUILIBRIUM EQUATION FOR IONS. OSTWALD'S "DILUTION LAW."

Let us take a substance AB , which in solution partially dissociates into 2 ions, A' (cation) and B' (anion), according to the equation—



Now, knowing that substances in solution behave in an analogous manner to gases, we apply the law of mass action, and find the equilibrium constant K given by—

$$\frac{[\text{A}'] \times [\text{B}']}{[\text{AB}]} = K$$

(Where square brackets denote concentration terms. The equilibrium is reached instantaneously.)

Since the reaction is a dissociation it is more usual to call K the dissociation constant. Further, the concentrations of cation and anion are equal, since the solution must be electrically neutral. If we consider the case in which one mole of the

original solute has been dissolved in v litres, and has undergone dissociation to the extent α , *i.e.* there are $(1 - \alpha)$ undissociated molecules and α cations and α anions, the mass action expression becomes—

$$\frac{\frac{\alpha}{v} \cdot \frac{\alpha}{v}}{1 - \alpha} = \frac{\alpha^2}{(1 - \alpha)v} = K$$

K should be independent of v (the dilution), but, of course, dependent upon temperature.

Now writing $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, the above expression may be put in the form—

$$\frac{\Lambda_v^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)v} = K$$

This equation in a slightly different form was first put forward by Ostwald in 1888 (*Zeitsch. physik. Chem.*, 2, 36), who gave to it the name of the *dilution law*. It was investigated at greater length by Ostwald in a later paper (*ib.* 2, 270, 1888) as regards its applicability to acids in aqueous solution. The following example, already given in part, is taken from Ostwald's paper :—

ACETIC ACID AT 25° C.

Volume of solution containing one gram molecule of solute v (liters).	α .	$\alpha \times 100$.	$\frac{\alpha^2}{(1 - \alpha)v} = K$.
8	4.34	1.193	0.04180
16	6.10	1.673	0.04179
32	8.65	2.380	0.04182
64	12.09	3.33	0.04179
128	16.99	4.68	0.04179
256	23.82	6.56	0.04180
512	32.20	9.14	0.04180
1024	46.00	12.66	0.04177
	$\Lambda_\infty = 364$		Mean value, $K = 0.0418$

The constancy in K is very good, the value being independent of v .

Reference may also be made to later papers upon the same subject (Ostwald, *Zeitsch. physik. Chem.*, 3, 170, 241, 369, 1889; Bredig, *ibid.*, 13, 289, 1894). A few typical illustrations may be given.

PROPIONIC ACID, AT 25° C.

v liters.	Δ .	100 α .	K.
8	3.65	1.016	0.0,130
16	5.21	1.452	0.0,134
32	7.36	2.050	0.0,134
64	10.39	2.895	0.0,135
128	14.50	4.04	0.0,133
256	20.38	5.68	0.0,133
512	28.21	7.86	0.0,131
1024	38.73	10.79	0.0,128
	$\Lambda_{\infty} = 359$		Mean 0.0,134

SUCCINIC ACID, AT 25° C.

v .	Δ . ¹	100 α .	K.
16	11.40	3.20	0.0,662
32	16.03	4.50	0.0,662
64	22.47	6.32	0.0,667
128	31.28	8.80	0.0,664
256	43.50	12.24	0.0,668
512	59.51	16.75	0.0,659
1024	81.64	22.95	0.0,668
2048	109.5	30.82	0.0,671
	$\Lambda_{\infty} = 355$		Mean 0.0,665

Ostwald succeeded in confirming the dilution law for 250 acids. These were all weak acids. Similarly, Bredig found the law applicable in the case of 50 bases investigated by him.

¹ Succinic acid only splits off one H⁺ until great dilution is reached, *i.e.* it acts as a monobasic acid. The conductivity values are actually molecular conductivity, which is identical in this case with equivalent conductivity.

By way of illustration, Bredig's results for ammonia and methylamine at 25° C. are given here—

AMMONIA.

<i>v</i> litres.	Λ .	$100 \times \alpha$.	K.
8	3.20	1.35	2.3×10^{-5}
16	4.45	1.88	2.3
32	6.28	2.65	2.3
64	8.90	3.76	2.3
128	12.63	5.33	2.3
256	17.88	7.54	2.4
	$\Lambda_{\infty} = 237$		Mean 2.3×10^{-5}

METHYLAMINE.

<i>v</i> litres.	Λ .	$100 \times \alpha$.	K.
8	14.1	6.27	5.2×10^{-4}
16	19.6	8.71	5.2
32	27.0	12.0	5.1
64	36.7	16.3	5.0
128	49.5	22.0	4.9
256	65.4	29.1	4.7
	$\Lambda_{\infty} = 225$		Mean 5.0×10^{-4}

Bredig remarks that the probable source of the decrease in K in the last case is due to some CO₂, which, of course, affects the result the more the greater the dilution. It will be noted that the K for methylamine is twenty times greater than that for ammonia, *i.e.* methylamine is the stronger base. At similar dilutions the CH₃NH₂ (*i.e.* CH₃NH₃OH) is more dissociated than ammonia (cf. the α column). For these substances, which are only slightly dissociated, *the ratio of the degrees of dissociation of the substances at the same dilution is given by the ratio of the square root of the dissociation constants.*

Thus

$$K_{\text{NH}_3\text{OH}} = \frac{\alpha^2}{(1 - \alpha)v}$$

and since α is very small compared to unity, we may write—

$$K_{\text{NH}_4\text{OH}} = \frac{\alpha^2}{v}$$

Similarly,
$$K_{\text{CH}_3\text{NH}_3\text{OH}} = \frac{\alpha_1^2}{v},$$

and hence,
$$\frac{\alpha}{\alpha_1} = \sqrt{\frac{K_{\text{NH}_4\text{OH}}}{K_{\text{CH}_3\text{NH}_3\text{OH}}}}$$

Besides the investigations of Ostwald and Bredig, a large number of other substances have been investigated (notably by Walker and his pupils) with the result that the dilution law, which is simply the law of mass action applied to the equilibrium of undissociated molecules and ions, has been verified in several hundred instances (see Lunden, *Ahrens Sammlung*, vol. 14).

An interesting phenomenon was noticed and explained by Ostwald in connection with the dissociation of the dibasic organic acids, *e.g.* malonic acid $\text{CH}_2(\text{COOH})_2$, succinic acid CH_2COOH

$\begin{array}{c} | \\ \text{CH}_2\text{COOH} \end{array}$, etc. These contain two carboxyl groups, and

there is the possibility, therefore, of dissociation giving 2 H^+ ions. It was found, however, that the ordinary dilution law, which only assumes a binary dissociation, X' and H^+ , holds good for these dibasic acids up to very considerable dilution. It follows, therefore, that both H atoms are not split off as ions with the same ease, but that after one has left the molecule the remaining one is retained until the dilution is great. Ostwald finds an explanation of this in the presence of the negative charge on the univalent anion which makes more difficult the addition of a second negative charge, owing to the electrostatic law that like charges repel one another. In the following table some examples are given of the dissociation of such acids, the final column containing the values of the degree of dissociation α , which are reached before the ordinary dilution law begins to break down, *i.e.* to no longer give a constant, thereby indicating the splitting off of the second H^+ ion. The position of the (COOH) groups in

the molecule is of great importance, for it is evident that the electrostatic action must be greater the nearer are the negatively charged carboxyl "rests" to one another, so that in those cases in which the carboxyl groups are close together the second-stage dissociation takes place only at very high dilutions. Thus, in the case of maleic acid the carboxyl groups are contiguous, and the dilution has to be carried to the region at which the first-stage dissociation is practically complete (about 93 per cent.) before the second-stage dissociation begins to manifest itself. Compare this with fumaric acid, in which the carboxyl groups are farther apart, and the second-stage dissociation begins to be noticeable when the first stage has reached 50 per cent. Of course, one must assume that the second stage does commence even at the higher concentrations, but is negligibly small.

Acid.	Dilution v in liters at which second stage dissociation manifests itself.	Degree of first stage dissociation reached at dilution v .
Malonic— $\text{CH}_2(\text{COOH})_2$	256	0.46–0.58
Tartaric— CHOHCOOH CHOHCOOH	128	0.30–0.04
Maleic— $\text{H}-\text{C}-\text{COOH}$ $\text{H}-\text{C}-\text{COOH}$	>1024	>0.93
Fumaric— $\text{H}-\text{C}-\text{COOH}$ $\text{COOH}-\text{C}-\text{H}$	256	0.40–0.50

It will be observed that on the average the first stage dissociation proceeds to the extent of 50 per cent. before the second stage dissociation becomes apparent.

"THE ANOMALY OF STRONG ELECTROLYTES."

The electrolytes referred to in the previous section are all weak electrolytes. The most remarkable phenomenon in

the equilibria relations of electrolytes in aqueous solution is that all (or nearly all) strong electrolytes—throughout the range of dilution 10–1000 litres—do not even approximately obey the dilution law. A few appear to do so, at least over a certain range of dilution, notably, amongst acids, dichloroacetic acid, cyanacetic acid, and maleic acid, but these instances are relatively few in number.¹ All the ordinary inorganic salts (with the exception of cadmium and mercury (*ic*), halides, mercuric cyanide, and one or two ferric salts), all the ordinary inorganic acids and bases (with the exception of weak acids, such as H_2S , H_3BO_3 , CO_2 , HNO_2 , SO_2 , phosphorous acids, and NH_3) dissociate in such a manner that when one calculates the “constant” for each dilution,² it is found that the resulting numbers scarcely remain even of the same order of magnitude.

Thus, taking the case of NH_4Cl at 18°C. , which we have already cited, a calculation of the “constant” gives the following values for “K” :—

$\text{NH}_4\text{Cl.}$

$v.$	$\Lambda.$	$\alpha.$	Ostwald, “K.”
1	90.7	0.750	2.2
2	94.8	0.784	1.4
10	103.5	0.856	0.51
20	107.8	0.892	0.37
100	114.2	0.945	0.16
500	118.0	0.976	0.08
1,000	119.0	0.985	0.065
5,000	120.4	1.000	—
10,000	120.9	“	—
50,000	120.9	“	—

The “constant” increases rapidly as the concentration increases. If, therefore, we assume that the law is obeyed at very great dilution (*i.e.* when $v = 1000$), we could conclude

¹ For further instances of acids see Abegg's *Electrolytic Dissociation Theory*.

² “ α ” being calculated from conductivity data.

that some effect comes in which causes the dissociation to be too great at the greater concentrations. This may not be the case, however. The values for " α " were obtained by the conductivity method $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$. The problem therefore resolves itself into this—is the law of mass action in error (*i.e.* not wide enough in its scope in its present simple form) or does the ratio of the equivalent conductivity at v to Λ_∞ not give a *true* measure of the dissociation? This point has not yet been settled.

In general the value of α obtained from cryoscopic (freezing-point) or ebullioscopic (boiling-point) measurements agree fairly closely with those obtained from conductivity measurements, where such comparison is possible. It should be remembered, however, that the degree of accuracy reached by the freezing- or boiling-point method is much less than it is in the case of conductivity measurements.

On the other hand, there is nothing in the derivation of the dilution law which would lead us to suppose that it would hold only for the limiting case of very small dissociations, *e.g.* weak electrolytes. One would have expected it to hold for strong electrolytes as well. Abegg, in his *Electrolytic Dissociation Theory* (p. 126), favours the view that the dilution law, *i.e.* the law of mass action, is in essence correct, and a constant would be obtained in the case of strong electrolytes as well as for weak, if we possessed the true values of the dissociation. He considers that the discrepancies are due to secondary efforts entering in, such as complex formation among the ions themselves (which is known to exist, for example, in the case of cadmium salts), or, on the other hand, to the formation of ion hydrates, *i.e.* combination of the solvent with the ions.

For a critical review of the question the reader should consult a paper by Noyes (*St. Louis Congress Report*, 1904), which also appeared in *Science*, 20, 577, 1904.

One point still remains to be mentioned in connection with the conductivity method of determining the dissociation. Drucker (*Zeitsch. physik. Chem.*, 49, 563, 1904) was the first

to emphasise that the principle may be correct, but the results in error because of error in the value for Λ_{∞} , and he also showed that a relatively small change in this value has very marked effect. He illustrated this with dichloroacetic and trichloroacetic acids. Jahn took up the same point (*Zeitsch. physik. Chem.*, 50, 129, 1904), illustrating it by the alkali salts.¹ Thus, taking Kohlrausch's value for the Λ_{∞} for KCl, viz. 129.07, and using this to calculate α and "K," the following results are obtained:—

KCl.

Concentration (C) grammoles per liter.	α .	Actual concentration of the ions = $C \times \alpha$.	"K."
0.1	0.8680	0.08680	0.571
0.05	0.8968	0.04484	0.390
0.02	0.9295	0.01859	0.245
0.01	0.9486	0.009486	0.175
0.005	0.9638	0.004819	0.128
0.002	0.9785	0.001957	0.0895
0.001	0.9866	0.0009866	0.0726

It is only necessary, however, to alter the value of Λ_{∞} from 129.07 to 127.65 (a quite empirical change, of course) to bring at least the *most dilute* solutions into approximate accord with the dilution law; thus—

C.	α .	$C \times \alpha$.	K.
0.01	0.9591	0.009591	0.225
0.005	0.9746	0.004873	0.187
0.002	0.9895	0.001979	0.187

The same conclusion holds for other strongly dissociated salts. Jahn corroborated this conclusion, using the freezing-point method with great care and accuracy. His results were

¹ See also Flugel, *Zeitsch. physik. Chem.*, 79, 586, 1912.

published (*Zeitsch. physik. Chem.*, 59, 31, 1907) after his death in a paper edited by Nernst. It thus appears that *Ostwald's Dilution Law holds in the limiting cases both when the dissociation is very small and when it is extremely great*. For intermediate values it appears to break down—though its failure may after all not be inherent in itself.

For an account of the anomalies of strong electrolytes, the reader should consult Drucker's article "On the Anomalies of Strong Electrolytes" (*Ahrens Sammlung*, vol. 10, 1905).

Although Ostwald's Dilution Law does not hold in general for strong electrolytes throughout the ordinary range of dilution ($v = 10$ to $v = 1000$), two other dilution laws have been found to give a constant for binary electrolytes. These, however, differ essentially from that of Ostwald, in that they are absolutely empirical, *i.e.* they are not deduced from the law of mass action. One is due to Rudolphi—and hence called Rudolphi's Dilution Formula (*Zeitsch. physik. Chem.*, 17, 385, 1895). It has the form—

$$\frac{\alpha^2}{(1 - \alpha)\sqrt{v}} = \text{constant.}$$

It thus differs from Ostwald's expression in having \sqrt{v} substituted arbitrarily for v . The constancy of the K is illustrated for the case of ammonium chloride at 18° C.—

v .	$\frac{\alpha^2}{(1 - \alpha)\sqrt{v}}$
10	1.55
20	1.56
100	1.47
500	1.46
1000	1.47
1667	1.60
5000	1.53
	Mean 1.51

A second empirical formula is due to van 't Hoff (*Zeitsch. physik. Chem.*, 18, 301, 1895). It may be written—

$$\frac{\alpha^{\frac{3}{2}}}{(1 - \alpha)\sqrt{v}} = \text{constant}$$

or

$$\frac{\alpha^3}{(1 - \alpha)^2 v} = \text{constant}$$

that is—

$$\frac{(\text{concentration of either of the ions})^3}{(\text{concentration of undissociated substance})^2} = \text{constant}$$

It will be observed that Ostwald's Dilution Law states—

$$\frac{(\text{concentration of either of the ions})^2}{(\text{concentration of undissociated substance})} = \text{constant}$$

The following table indicates the values of the van 't Hoff constant for a few strong electrolytes at 18° C.

v .	KNO ₃ .	MgSO ₄ .	HCl.	KCl.	NaCl.	KBr.
2	1.63	—	4.41	2.49	1.87	2.44
4	1.67	0.162	4.87	2.23	1.71	2.55
8	1.68	0.156	4.43	2.1	1.6	2.28
16	1.72	0.151	4.72	1.94	1.4	2.38
32	1.82	0.151	5.29	1.87	1.43	2.41
64	1.88	0.158	—	1.72	1.38	2.72

An attempt to give an approximate "physical" significance to van 't Hoff's formula was made by Kohlrausch (*Zeitsch. physik. Chem.*, 18, 662, 1895). Denoting by C_i the concentration of each of the ions, by C_s the concentration of the undissociated substance, van 't Hoff's formula may be written

$$\frac{C_i^3}{C_s^2} = \text{constant, and therefore } \frac{C_i}{C_s^{\frac{2}{3}}} = \text{constant} = k_2, \text{ say. This}$$

may also be put in the form—

$$\frac{C_i}{C_s} = \frac{k_2}{C_s^{\frac{1}{3}}}$$

Now $C_s^{\frac{1}{3}}$ is the "linear density" of the undissociated molecules, or $C_s^{-\frac{1}{3}}$ is the mean distance apart of the undissociated molecules. Calling this distance r_s , the above expression may be written—

$$\frac{C_i}{C_s} = k_2 r_s$$

$$\text{or } \frac{\text{concentration of either ion}}{\text{concentration of undissociated substance}} = \begin{cases} \text{constant} \times \text{the} \\ \text{distance of} \\ \text{the molecules} \\ \text{apart} \end{cases}$$

It must be borne in mind that there is no theoretical reason why either the Rudolphi or the van 't Hoff expression should yield a constant at all. Other expressions, also empirical or semi-empirical, have been proposed from time to time. Attention may be drawn to two of these which have a certain amount of theoretical basis, first, that proposed by Partington (*Trans. Chem. Soc.*, 97, 1158, 1910), viz.—

$$\frac{\alpha^2}{(1 - \alpha)(v + \rho\alpha)} = K$$

where α denotes the degree of dissociation at the dilution v , and ρ is a constant which has to be determined by experiment; and, secondly,¹ the expression proposed by Kendall (*Trans. Chem. Soc.*, 101, 1283, 1912), viz.—

$$\frac{\alpha^2}{(1 - \alpha)v} = k + c \frac{1 - \alpha}{\alpha}$$

where c is a constant which has also to be determined by experiment.

Partington's expression holds only very approximately for strong electrolytes, the constant passing through a maximum. Further, Partington's expression reduces to that of Ostwald in the limit when α is small compared to unity. It leaves the question still open, however, whether the law of mass

¹ Partington has shown recently that Kendall's formula is a particular case of his own expression (*Proc. Chem. Soc.*, 1914).

action in principle is applicable to electrolytic dissociation when the latter is large.

ISOHYDRIC SOLUTIONS

When we mix two electrolytic solutions together, we cannot in general calculate the conductivity of the mixed solutions from those of the components by the simple mixture law, since each dissolved substance affects the dissociation of the other, and thus alters the total number of ions present. There must be, however, certain solutions for which the mixture law does hold, *i.e.* the dissociation of each solution is not altered on mixing. These are called isohydric solutions. The experimental method of testing for isohydry is by determining the conductivity (a or b) of each solution separately, and likewise that of the resultant mixture (A). Isohydry obtains if the mixture law holds good, *i.e.* if the observed value—

$$A = a \frac{v_a}{v_a + v_b} + b \frac{v_b}{v_a + v_b}$$

where v_a and v_b are the volumes of each separate solution, and the dilution is sufficiently great to warrant writing the final mixture volume as simply $v_a + v_b$. A solution of, say, $\frac{N}{10}$ concentration would comply with such a condition, and at the same time the degree of dissociation would not necessarily be complete—for weak electrolytes, the dissociation at this concentration would be very small indeed; for strong electrolytes, it might be about 80 per cent.

Now what is the theoretical condition for isohydry—that is, what is the condition that on mixing two solutions no change in the dissociation of each may arise—a state of things which is shown to exist by the mixture law holding for the conductivity?

Let us take two solutions, one containing the acid HA , the other containing the acid HA_1 . Let the volume of the first be v_a and that of the second be v_b . Suppose the degrees of dissociation are respectively α_a and α_b . If both acids are weak,

they obey Ostwald's dilution law. That is to say, for HA we have—

$$\frac{\alpha_a^2}{(1 - \alpha_a)v_a} = k_a \quad . \quad . \quad . \quad . \quad (1)$$

and for HA₁ we have—

$$\frac{\alpha_b^2}{(1 - \alpha_b)v_b} = k_b \quad . \quad . \quad . \quad . \quad (2)$$

Now let us assume that these solutions are actually isohydric, that is to say, that on mixing them it is found that the mixture law holds for the observed specific conductivity when this is expressed in terms of the separate conductivities of each, assuming that their respective degrees of dissociation are the same before and after mixing. Since the solutions are supposed to be fairly dilute, there will be no contraction or other chemical effect coming in, and the total final volume is $v_a + v_b$.

Under these conditions the mass of hydrogen ion is $\alpha_a + \alpha_b$, and applying the dilution law to the case of the acid HA in the mixture, we get—

$$\frac{(\alpha_a + \alpha_b)\alpha_a}{(1 - \alpha_a)(v_a + v_b)} = k_a \quad . \quad . \quad . \quad . \quad (3)$$

Dividing (3) by (1), we get—

$$\frac{(\alpha_a + \alpha_b)v_a}{(v_a + v_b)\alpha_a} = 1$$

$$\text{or} \quad \frac{\alpha_a + \alpha_b}{\alpha_a} = \frac{v_a + v_b}{v_a}$$

$$\text{whence} \quad \frac{\alpha_b}{\alpha_a} = \frac{v_b}{v_a}$$

$$\text{or} \quad \frac{\alpha_b}{v_b} = \frac{\alpha_a}{v_a}$$

But $\frac{\alpha_b}{v_b} = \left\{ \begin{array}{l} \text{concentration of H}^+ \text{ ion in the solution of the} \\ \text{acid HA}_1 \text{ by itself} \end{array} \right.$

likewise $\frac{\alpha_a}{v_a} = \left\{ \begin{array}{l} \text{concentration of H}^+ \text{ ion in the solution of the} \\ \text{acid HA by itself} \end{array} \right.$

Therefore, we find that when solutions are isohydric they each contain the common ion—in this case the hydrogen ion—at the same concentration. We may apply this conclusion of the electrolytic dissociation theory in the reverse sense, *i.e.* if we make two solutions containing a common ion so that the common ion has the same concentration value in both, then the dissociation of each of these solutions will be unaltered upon mixing them together in *any proportions*.

We thus are dealing with what at first sight is rather a remarkable phenomenon, *viz.* that although the volume of the system—say the HA_1 solution—is increased by addition of HA_2 solution, the dissociation of each of these acids is unchanged. Here we have apparently an instance of degree of dissociation being independent of dilution. It must be remembered, however, that there is in reality no disagreement with the principle of dissociation progressing with dilution, for by dilution in the ordinary sense is meant increase in volume due to addition of pure solvent alone. Further, it does not matter what amount of the second solution we may add, provided the solutions are isohydric. The first investigation upon isohydry and the demonstration that such exists is that of Arrhenius (*Wiedemann's Annalen*, 30, 54, 1887). His work was extended in a later paper (*Zeitsch. physik. Chem.*, 2, 284, 1888), from which the following table is taken. A number of solutions of different acids were prepared of such concentrations that the specific conductivity of any mixture of two was given quantitatively by the mixture law. Arrhenius then calculated from the conductivity of each separate solution what the degree of dissociation was, and thence the hydrogen ion concentration in each case. The values for the hydrogen ion concentration of each of the single acids at various dilutions (these dilutions being such that the mixture law applied to them when mixed) are given in the horizontal columns, and it will be seen that the solutions contain almost the same amount of hydrogen ion. In the table the concentration terms are milligrams per liter.

HCl:	(COOH) ₂ .	C ₄ H ₆ O ₆ Tartaric.	HCOOH.	CH ₃ COOH.	Mean value for [H ⁺].
151·5	152·6	—	—	—	152·1
42·3	35·1	—	—	—	38·7
22·03	21·37	19·07	—	—	20·82
4·48	4·09	4·17	4·42	3·96	4·18
1·33	1·24	1·25	1·44	1·33	1·32
0·379	0·397	0·381	—	0·402	0·390

Again, it will be remembered in deducing the equivalence of the concentration of the common ion in the case of isohydric solutions as a consequence of the electrolytic dissociation theory, we only made use of general volume terms v_a and v_b . The formation of isohydric solutions, therefore, should not depend upon the addition of any particular volume of the second solution to the first. That is to say, the mixture law should be obeyed for any case when once it has been shown to hold for the special case viz.: a mixture formed of equal volumes ($v_a = v_b$). Arrhenius (*l.c.*, 1887) has verified this in a number of instances. He found, for example, that a solution of H_3PO_4 , specific conductivity (in reciprocal mercury resistance units) $223·7 \times 10^{-8}$, is isohydric with a solution of HCl, specific conductivity $167·4 \times 10^{-8}$ (by the method of trial and error, using equal volumes of each acid, so that the specific conductivity, as calculated by the mixture law, took the simple shape $A = \frac{a + b}{2}$). He now mixed these in *different* volume proportions, with the following result:—

	Specific conductivity.	
	Observed.	Calculated.
7·5 c.c. H_3PO_4 solution + 2·5 c.c. HCl solution	$209·5 \times 10^{-8}$	$209·9 \times 10^{-8}$
5·0 c.c. " " + 5·0 c.c. " "	$195·1 \times 10^{-8}$	$195·6 \times 10^{-8}$
2·5 c.c. " " + 7·5 c.c. " "	$181·7 \times 10^{-8}$	$181·2 \times 10^{-8}$

The calculated conductivity is the result given by the mixture law expression—

$$\left[a \frac{v_a}{v_a + v_b} + b \frac{v_b}{v_a + v_b} \right]$$

The agreement between the last two columns bears out the theoretical conclusion. Even closer agreement was obtained in the case of mixtures of oxalic acid and acetic acid, as likewise for mixtures of acetic acid and hydrochloric acid. A few of the data obtained in the latter case are given here.

It was found (by mixing equal volumes and altering the concentration of the acids singly) that a solution of acetic acid, specific conductivity 12.18×10^{-8} , was isohydric with a solution of HCl, specific conductivity 14.54×10^{-8} . These solutions were then mixed in different volume proportions, as follows :—

	Specific conductivity.	
	Observed.	Calculated.
10 c.c. CH ₃ COOH solution + 1 c.c. HCl solution	12.37×10^{-8}	12.39×10^{-8}
10 c.c. " " + 4 c.c. " "	12.87×10^{-8}	12.85×10^{-8}
10 c.c. " " + 7 c.c. " "	13.18×10^{-8}	13.15×10^{-8}
10 c.c. " " + 15 c.c. " "	13.58×10^{-8}	13.59×10^{-8}
5 c.c. " " + 10 c.c. " "	13.81×10^{-8}	13.76×10^{-8}
1 c.c. " " + 10 c.c. " "	14.34×10^{-8}	14.33×10^{-8}

It is rather remarkable that the above independence of volume, which was theoretically predicted on the basis of the dilution law (*i.e.* the law of mass action) which holds for weak electrolytes alone, should have been also verified for mixtures containing strong acids such as hydrochloric.

We may now draw attention to a result which is indeed almost self-evident, namely, that solutions which are isohydric with one and the same solution are isohydric with one another. Arrhenius verified this in the case of a number of acids.

While it is in general possible to prepare isohydric solutions—the criterion for isohydric being that the conductivity

in the case of the resulting mixture obeys the mixture law—it is occasionally found impossible to do so. Thus let us take a solution of $\text{HCl } \frac{N}{42}$ (Arrhenius, *l.c.*, 1887), and we require to find the corresponding isohydric acetic acid solution. Arrhenius had previously found that 1N acetic was isohydric with $\frac{1}{220}$ N HCl . The acetic sought for in the present case must be still stronger than 1N. Experimentally the following differences were found between the observed conductivity A for the mixture and the value calculated by the mixture law:—

1N acetic	gave a difference	— 19.0
2.5	„ „	— 24.4
5	„ „	— 33.3
10	„ „	— 50.0

On increasing the acetic acid content, therefore, instead of reaching a point where the above difference will vanish, we find this difference steadily increasing. The conductivity of acetic acid goes through a maximum and then falls instead of increasing continuously with the concentration. This effect is due to the increased friction owing to the large number of undissociated molecules which are present along with the ions at the higher concentration. It is found impossible to reach a high enough value for the specific conductivity in the case of the acetic acid solution such that the value given by the mixture law when the mixture is made approximates to the observed conductivity. Even the maximum value of the acetic acid is too low. The remarkable fact, however, is that we must suppose it quite possible that solutions of CH_3COOH of the same H^+ ion concentration as $\frac{N}{42}$ HCl can be prepared, and that, therefore, isohydric solutions can be obtained if we look upon equality of the H^+ ion as the criterion of isohydry. The apparent anomaly is due to the fact that the conductivity of concentrated CH_3COOH solutions is not the correct measure of the H^+ ion concentration, *i.e.* we

cannot write $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, since the mobilities are no longer the same at the dilution v as they are at infinite dilution.

We now pass on to the application of the principle of isohydry to solutions which consist of mixtures of several substances in equilibrium. We introduce the idea of an imaginary septum or imaginary septa by which we can suppose the mixture divided up into isohydric solutions of the constituent electrolytes. Thus, if we take a dilute mixture of NaCl and KCl, these substances are dissociated practically to the same degree at the same dilution, so that we might imagine the septum dividing the solution into two equal parts, one part containing only KCl the other only NaCl, the solutions being isohydric. In the case of the mixture of a solution of sodium acetate (which is largely dissociated), and acetic acid (which is only slightly dissociated), the septum would no longer be placed so as to divide the whole solution in half in order to get the acetanion $\text{CH}_3\text{COO}'$ concentration equal on both sides, but would lie far over towards the acetic acid side.

It is evident that we can regard any mixture of the two acids as composed of such quantities of each pure acid solution as are isohydric with one another. This case may be treated in the following way.¹

In the mixture suppose c_1 to be the total concentration of the acid HA_1 , c_2 that of HA_2 , $[\text{H}^*]$ the total concentration of H^* ions (determined, say, by their catalytic effect upon the inversion of cane sugar), and finally α_1 and α_2 the degrees of dissociation of the acids (which are supposed to obey the dilution law). We have then the following relations :—

$$k_1 = \frac{[\text{H}^*][\text{A}'_1]}{[\text{HA}_1]} = \frac{[\text{H}^*]\alpha_1 c_1}{(1 - \alpha_1)c_1} = [\text{H}^*] \frac{\alpha_1}{1 - \alpha_1}$$

Similarly,

$$k_2 = \frac{[\text{H}^*][\text{A}'_2]}{[\text{HA}_2]} = [\text{H}^*] \frac{\alpha_2 c_2}{(1 - \alpha_2)c_2} = [\text{H}^*] \frac{\alpha_2}{1 - \alpha_2}$$

¹ In this discussion I have followed closely the treatment given by Abegg, *Electrolytic Dissociation Theory*, p. 63 seq.

from which we obtain—

$$\frac{1}{a_1} = 1 + \frac{[H^*]}{k_1} \quad \frac{1}{a_2} = 1 + \frac{[H^*]}{k_2}$$

The sought-for concentrations x_1 and x_2 of the pure solutions, whose degrees of dissociation are also a_1 and a_2 , are given by the relations—

$$k_1 = \frac{a_1^2 x_1}{1 - a_1} \quad \text{or} \quad x_1 = k_1 \frac{1 - a_1}{a_1^2}$$

$$k_2 = \frac{a_2^2 x_2}{1 - a_2} \quad \text{or} \quad x_2 = k_2 \frac{1 - a_2}{a_2^2}$$

On substituting in these two equations the values for k_1 and k_2 found above, we obtain—

$$x_1 = [H^*] \frac{a_1}{1 - a_1} \cdot \frac{1 - a_1}{a_1^2} = [H^*] \frac{1}{a_1}$$

and
$$x_2 = [H^*] \frac{1}{a_2},$$

or, on substituting k_1 and k_2 respectively—

$$x_1 = [H^*] \left\{ 1 + \frac{[H^*]}{k_1} \right\} = [H^*] + \frac{[H^*]^2}{k_1}$$

$$x_2 = [H^*] \left\{ 1 + \frac{[H^*]}{k_2} \right\} = [H^*] + \frac{[H^*]^2}{k_2}$$

in place of which, for small k values, the approximation usually suffices—

$$x_1 = \frac{[H^*]^2}{k_1} \quad \text{and} \quad x_2 = \frac{[H^*]^2}{k_2}$$

or
$$\frac{x_1}{x_2} = \frac{k_2}{k_1}$$

That is, two acids upon being mixed will not affect each other's dissociation provided their separate concentrations are such as to be inversely proportional to their dissociation constants.

CONSIDERATION OF THE CASE IN WHICH THE ACIDS DO
AFFECT THEIR MUTUAL DEGREE OF DISSOCIATION.

The effect of addition of an acid to the solution of another.—Let us denote the first acid by HA_1 and the second by HA_2 . Let the corresponding dissociation constants be k_1 and k_2 (measured for each acid separately).

Let c_1 and c_2 be the total concentration of each acid in the mixture, and when in the mixed state let the degrees of dissociation be respectively a_1 and a_2 .

In the mixture—

The concentration of the H^+ ions $= a_1c_1 + a_2c_2$

„ „ A_1 „ $= a_1c_1$

„ „ A_2 „ $= a_2c_2$

and therefore we have, applying Ostwald's Dilution Law—

$$k_1(1 - a_1)c_1 = a_1c_1(a_1c_1 + a_2c_2)$$

$$k_2(1 - a_2)c_2 = a_2c_2(a_1c_1 + a_2c_2)$$

Now if the acids are both weak and at moderate dilutions, a_1 and a_2 may be neglected compared to $(1 - a_1)$ and $(1 - a_2)$, i.e. $(1 - a_1) = (1 - a_2)$ approximately. Hence in this case—

$$\frac{k_1}{k_2} = \frac{a_1}{a_2}$$

That is to say, the actual degree of dissociation which each possesses when mixed is proportional to the respective dissociation constant.

Hence the acid with the larger dissociation constant will be dissociated to the larger extent in the mixture. The most interesting case is, however, when we add a strong acid—say, HCl —to a solution of a weak acid—say, acetic—and investigate what happens. Calling k_1 the dissociation constant of acetic acid, and with the same notation as before—

$$k_1 = \frac{a_1}{1 - a_1}(a_1c_1 + a_2c_2)$$

we can write, as before, $(1 - a_1) = 1$, with even greater exactness, for now, owing to the addition of the strong acid, we

have added a large quantity of H^+ ions, and therefore have thrown back the dissociation of the weak acid. This must necessarily happen if the weak acid obeys the dilution law, for the product of the concentrations of the two ions divided by the concentration of the undissociated molecules, must be constant under all circumstances. For the sake of simplicity, let us assume in the above case that the dissociation of the HCl is complete, *i.e.* $\alpha_2 = 1$. Then we have—

$$k_1 = \alpha_1(\alpha_1 c_1 + c_2) = \alpha_1^2 c_1 + \alpha_1 c_2$$

Now α_1 (the degree of dissociation of the weak acid) is a small number much less than unity. The higher power may, therefore, be neglected compared to terms containing the first power, that is—

$$k_1 = \alpha_1 c_2$$

or

$$\alpha_1 = \frac{k_1}{c_2}$$

In words the degree of dissociation (α_1) of the weak acid in the mixture is directly proportional to its dissociation constant, and inversely as the concentration of the strong acid. By adding a large quantity of HCl , therefore, to acetic acid solution, we can cause the acetic acid dissociation practically to vanish, *i.e.* there is practically no acetanion in the solution. The same behaviour is noticed in the case of bases, and, further, instead of adding strong acids (or strong bases), we may also add salts which are likewise strongly dissociated. Thus, in analytical chemistry, the case occurs in which we add NH_4Cl to NH_3 solution before employing it to precipitate certain hydroxides. The effect of the NH_4Cl is to drive back the dissociation of the NH_4OH so that extremely little OH' ion exists in solution. Owing to the very slight solubility of the hydroxides of metals such as Fe , Al , Zn , even the small quantity of OH' thus left is sufficient to yield hydroxide in excess of the solubility, but the OH' ion is not sufficient to form $Mg(OH)_2$ in quantities sufficiently great to exceed its much greater solubility, and hence this base is not precipitated, separation of magnesium being thereby effected. This problem belongs, however, to heterogeneous equilibrium and will be dealt with later.

As illustration of the phenomenon of throwing back the dissociation one may give a few measurements made by Arrhenius (1889) of the velocity of inversion of cane sugar by means of the H^+ ion of acetic acid, when varying quantities of sodium acetate are added (which, being a salt, is largely dissociated, and hence gives rise to large quantities of acetanion CH_3COO' , and this, in accordance with the principle of mass action, causes the H^+ ion from the acid to be diminished).

0.25 N ACETIC ACID + C NORMAL SODIUM ACETATE.

C = 0.	0.0125.	0.025.	0.05.	0.125.	0.25.	
velocity of reaction— observed	0.75×10^3	0.122×10^3	0.070×10^3	0.040×10^3	0.019×10^3	0.0105×10^3
velocity of reaction— calculated ¹	0.74×10^3	0.129×10^3	0.070×10^3	0.038×10^3	0.017×10^3	0.0100×10^3

THEORY OF THE DISTRIBUTION OF A BASE AMONG TWO OR MORE ACIDS.

Let us consider the distribution which takes place when a *strong* base BOH is added to a mixture of two *weak* acids, HA_1 and HA_2 , the quantity of base being insufficient to neutralise both acids completely. In 1 liter of solution suppose there are—

$$\begin{array}{lll}
 b & \text{moles of BOH} \\
 c_1 & \text{,,} & HA_1 \\
 c_2 & \text{,,} & HA_2 \\
 c_1 + c_2 & > b
 \end{array}$$

NOTE.—These terms do not represent *actual* concentration values, since reaction proceeds immediately the base is added. They only serve, therefore, to express the composition which the mixture would have if no reaction took place.

¹ This initial calculated value of the velocity constant is obtained as a result of other experiments on the catalytic effect of H^+ ion, which show that with moderate approximation the velocity of catalysis is directly pro-

Suppose, further, that a fraction x of each mole of the base reacts with the acid HA_1 , then $(1 - x)$ is the fraction of one mole of base which is left for the acid HA_2 . In the mixture we have, therefore, assuming complete dissociation of the salt—

bx molecules of salt BA_1 or bx moles of A'_1
 $b(1 - x)$ „ „ BA_2 or $b(1 - x)$ „ A'_2
 also $(c_1 - bx)$ moles of nearly undissociated acid HA_1
 $c_2 - b(1 - x)$ „ „ „ HA_2

If k_1 and k_2 are the respective dissociation constants of the acids, we have—

$$k_1 = \frac{[\text{H}^+][\text{A}'_1]}{[\text{HA}_1]} = \frac{[\text{H}^+]bx}{c_1 - bx}$$

$$k_2 = \frac{[\text{H}^+][\text{A}'_2]}{[\text{HA}_2]} = \frac{[\text{H}^+][b(1 - x)]}{c_2 - b(1 - x)}$$

so that
$$\frac{k_1}{k_2} = \frac{x}{1 - x} \cdot \frac{c_2 - b(1 - x)}{c_1 - bx}$$

or in words :

$$\frac{\text{concentration of salt } \text{BA}_1}{\text{concentration of salt } \text{BA}_2} = \frac{k_1 \times \text{concentration of acid } \text{HA}_1}{k_2 \times \text{concentration of acid } \text{HA}_2}$$

The distribution ratio $\frac{x}{1 - x}$ is thus a function of the dissociation constants of the competing acids—

The value of x is given by the following equation—

$$x = \left(\frac{k_1}{k_2} - 1 \right) b + \frac{k_1}{k_2} c_1 + c_2$$

$$\pm \sqrt{\left[\left(\frac{k_1}{k_2} - 1 \right) b + \frac{k_1}{k_2} c_1 + c_2 \right]^2 - 4 \left[\frac{k_1}{k_2} - 1 \right] \frac{k_1}{k_2} b c_1}$$

$$2 \left(\frac{k_1}{k_2} - 1 \right) b$$

The above relations can be simplified in certain cases.

portional to the H^+ ion. At the date of Arrhenius' measurements the catalytic effect of the undissociated molecule of acid was scarcely considered sufficiently. In the case of acetic acid, however, the effect of the molecule is small.

Thus, when we add one equivalent of the base to a mixture containing one equivalent of each acid, then $b = c_1 = c_2$, and—

$$\frac{k_1}{k_2} = \frac{x}{1-x} \cdot \frac{bx}{b(1-x)} = \frac{x^2}{(1-x)^2}$$

or
$$\frac{x}{1-x} = \sqrt{\frac{k_1}{k_2}}$$

To determine the distribution ratio, therefore, we have to determine the dissociation constant of each acid—if such a constant exists. The most usual method of determining k_1 or k_2 is by means of the electrical conductivity. Catalytic methods of estimating H^+ ion concentrations may also be employed.

In the case of *strong* acids which possess no dissociation constant, the preceding formula is inapplicable. In this case the most direct method is to actually carry out a distribution experiment according to the method of Thomsen (thermochemical method) or that of Ostwald (volume method). We may briefly consider these.

In order to compare the strengths of two acids, they must evidently be compared under the same conditions, the essential condition being secured when the reacting system is a single homogeneous phase, *e.g.* a solution. Thus it is known that HCl is a stronger acid than H_2SO_4 , yet by evaporating almost to dryness a solution of a chloride with H_2SO_4 present, it will be found that practically all the HCl has been expelled and replaced by H_2SO_4 in the salt, *i.e.* a sulphate is formed. The HCl is expelled, however, not because it is a weaker acid than H_2SO_4 , but because it is more volatile, and escapes during the heating process. To compare the strengths or “avidities” of two acids, we have to measure the distribution of a base between them, the base being insufficient for complete neutralisation of both.

The Thermochemical Method of Thomsen.—When one equivalent of H_2SO_4 is neutralised by caustic soda in dilute solution, there is heat evolved, say a cals. When one equivalent of HCl is neutralised by the same amount of $NaOH$, there is a quantity of heat, say b cals., evolved (b is not very different

from a , being a little smaller than a). Now take a solution containing one equivalent of Na_2SO_4 , and add one equivalent of HCl . Thomsen noted a small heat absorption of c calories. If there had been no chemical action at all, there would have been no heat evolved or absorbed. If the HCl had completely expelled the SO_4 and formed NaCl , there would have been a heat absorption of $(a - b)$ cals. Thus, we might think of the process occurring in two stages—first, a deneutralisation or liberation of *all* the H_2SO_4 , which would be accompanied by a heat *absorption* of a cals., and, secondly, a neutralisation of the HCl , which would be accompanied by an *evolution* of b cals., the process yielding a nett heat effect of $(a - b)$ cals. But a smaller heat absorption was noted, viz. c cals., where in this case c was about $\frac{11}{13}$ of $(a - b)$. If we assume that the amount of action is proportional to the heat effect, then the quantity of Na_2SO_4 , which was transformed into NaCl was $\frac{c}{a - b}$, or about $\frac{11}{13}$. A correction must, however, be introduced, because the H_2SO_4 liberated combines with some of the Na_2SO_4 to give bisulphate. Special experiments were carried out to measure this; it was found to be accompanied by an absorption of heat, so that the total heat absorbed in the previous experiment had been too great. When the correction is applied it is found that $\frac{c_{\text{corrected}}}{a - b} = \frac{2}{3}$ approx., or that HCl has appropriated $\frac{2}{3}$ of the base, leaving $\frac{1}{3}$ to the H_2SO_4 . So that under the same conditions exactly, HCl is twice as strong as H_2SO_4 .

Ostwald's Volume Method.—A solution of copper nitrate¹ had a volume 3847·4 c.c., and an equivalent solution of copper sulphate had a volume 3840·3 c.c. Solutions of nitric and sulphuric acids had respectively the volumes 1933·2 c.c. and 1936·8 c.c. If no action occurred on mixing the CuSO_4 solution with the HNO_3 solution, the total volume would be $3840·3 + 1933·2 = 5773·5$ c.c.; if *complete* transformation into copper nitrate and H_2SO_4 took place, the total final volume

¹ The data are quoted from Walker's *Introduction to Physical Chemistry*

would be $3847.4 + 1936.8 = 5784.2$ c.c. The actual volume found after mixing $\text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4$ solutions was 5780.3 c.c., and by mixing the $\text{CuSO}_4 + \text{HNO}_3$ solutions, 5781.3 c.c. The mean of the two (they should be identical if disturbing effects such as formation of acid salts were absent) is 5781.0 c.c. If *complete* transformation from $\text{CuSO}_4 + \text{HNO}_3$ into $\text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4$ had taken place, the volume increase would have been $5784.2 - 5773.5 = 10.7$ c.c. The observed volume increase was $5781 - 5773.5 = 7.5$ c.c. Hence there is a preponderating amount of $\text{Cu}(\text{NO}_3)_2$ formed, or, in other words, HNO_3 is a stronger acid than H_2SO_4 in the ratio of $7.5 : 3.2$; or nitric acid takes 70 per cent. of the base and sulphuric 30 per cent. Corrections analogous to those introduced into the thermochemical method alter this numerical result, the final values being that HNO_3 takes 60 per cent. of the base, H_2SO_4 40 per cent.

Ostwald's volume method is also applicable to the direct determination of $\frac{x}{1-x}$ for *weak* acids, and hence allows of verification of the relationship already obtained, since the numerical values of k_1 and k_2 can be obtained independently. This was carried out by Arrhenius, the following table containing a few of his results.

Distribution Ratio of a Base between two Acids. (Observations of Ostwald, 1878; theoretical calculation by Arrhenius, 1889)—

	Observed value.	Calculated value.
$\text{HNO}_3 : \text{CHCl}_2\text{COOH}$	0.76	0.70
$\text{HCOOH} : \text{CH}_3\text{COOH}$	0.76	0.77
$\text{HCOOH} : \text{C}_2\text{H}_5\text{COOH}$	0.79	0.81
$\text{CH}_3\text{COOH} : \text{C}_2\text{H}_5\text{COOH}$ (normal acid)	0.53	0.53
$\text{CCl}_3\text{COOH} : \text{HCOOH}$	0.97	0.96
$\text{CCl}_3\text{COOH} : \text{Cl}_2\text{CHCOOH}$	0.71	0.70
$\text{CCl}_3\text{COOH} : \text{CH}_2\text{ClCOOH}$	0.92	0.92

Further, if strong acids possessed dissociation constants, the numerical values of such constants would be large, since

large dissociation means a large value of k . Hence, when dissociation constants do not exist, an approximate idea of relative strength may be obtained from equivalent conductivity, since this gives a measure of α , the term Λ_{∞} being very nearly the same for all acids. Another method would be by comparison of the catalytic power of various acids upon a reaction sensitive to H^+ ion. That these effects are really proportional to one another was shown by Arrhenius. In the following table are given values of the equivalent conductivity and catalytic power referred to HCl set equal to 100. The relative acidity of any two acids, *i.e.* the value of $\frac{x}{1-x}$, is simply the ratio of the equivalent conductivities or catalytic effects of the acids considered.

Acid.	Velocity constant of catalysed reaction.	Equivalent conductivity.
Hydrochloric . . .	100	100
Nitric	96	99.6
Sulphuric	54	65.1
Oxalic	18	19.7
Acetic	0.4	0.4

HYDROLYSIS.

In the foregoing study of solutions we have regarded the water as simply inert. In reactions known as hydrolytic reactions water takes a stoichiometric part in virtue of its ions H^+ and OH' , which are present in extremely small but nevertheless, for certain cases, not negligible quantities. The electrolytic dissociation of water takes place according to the reaction—



It is thus quite analogous to the dissociation of a weak electrolyte.

The Ostwald constant in this case should be—

$$k = \frac{[H^+][OH']}{[H_2O]}$$

where the terms in brackets denote equilibrium concentration values, and k is the true dissociation constant of water. Since, however, in water by itself, or in dilute solutions in general, the concentration of the water molecules is sensibly constant, it is customary to transfer this constant term $[\text{H}_2\text{O}]$ into the term k , and write as the so-called dissociation constant of water, or better "the ionic product"—

$$K_w = [\text{H}^*][\text{OH}']$$

In pure water, or absolutely neutral solutions of salts, obviously $[\text{H}^*] = [\text{OH}']$, and we find for such cases that the concentration of either ion $= \sqrt{\text{ionic product}}$. As will be shown later, the numerical value for the concentration of either H^* or OH' in neutral solution is 1×10^{-7} gram-moles per liter. K_w is therefore of the order 10^{-14} .

We might now consider for a moment the ordinary dissociation of a weak acid—say, acetic acid, taking into consideration the dissociation of the solvent. According to the ordinary form of Ostwald's Dilution Law—

$$k_{\text{acid}} = \frac{[\text{H}^*][\text{A}']}{[\text{HA}]} \quad . \quad . \quad . \quad . \quad (1)$$

That is to say, in the aqueous solution of this acid we have the concentration of H^* ion possessing the value $[\text{H}^*]$, which is in general considerably larger than 10^{-7} gram-moles per liter, its value in pure water. But since we are considering a dilute solution, it follows that simultaneously we must have the following relationship satisfied—

$$K_w = [\text{H}^*][\text{OH}'] \quad . \quad . \quad . \quad (2)$$

Since $[\text{H}^*]$ is much greater than 10^{-7} moles per liter, and K_w is constant, it is obvious that $[\text{OH}']$ is much less than 10^{-7} .

Further, since the system is on the whole electrically neutral, it follows that the sum of the (+) ions = the sum of all the (−) ions.

Therefore
$$[\text{H}^*] = [\text{OH}'] + [\text{A}'] \quad . \quad . \quad . \quad . \quad (3)$$

that is
$$[\text{H}^*] = \frac{K_w}{[\text{H}^*]} + \frac{k_{\text{acid}} [\text{HA}]}{[\text{H}^*]}$$

or
$$[\text{H}^*]^2 = K_w + k_{\text{acid}} [\text{HA}]$$

This is really the strictly accurate form of the dissociation or dilution law. K_w , however, is in general negligible compared to $k_{\text{acid}} \times [\text{HA}]$, e.g. in a normal solution of acetic acid $[\text{HA}]$ is practically unity, owing to the small dissociation of the acid, $k_{\text{acid}} = 1.8 \times 10^{-5}$, while K_w is much smaller, viz. 1.2×10^{-14} . Neglecting K_w in the above expression, we get—

$$[\text{H}']^2 = k_{\text{acid}} [\text{HA}]$$

or

$$k_{\text{acid}} = \frac{[\text{H}']^2}{[\text{HA}]}$$

which is the ordinary form of Ostwald's Dilution Law. We have not yet, however, dealt with a hydrolytic reaction. The phenomenon of hydrolysis comes in when *we are dealing with a solution of a salt* (not the acid or base by itself), the acidic or basic or both components of which salt are *weak*. Let us consider a solution of sodium phenate. It dissociates into the ions—



Sodium hydroxide is, of course, a strong base, and it must be borne in mind that almost all salts dissociate very largely, whether their constituents are strong or weak. In, say, a normal solution of the above salt, we have thus “momentarily” a very large concentration of $\text{C}_6\text{H}_5\text{O}'$ ions, probably 0.75 N. Now phenol is an acid which dissociates according to the equation—



and the dissociation constant $\frac{[\text{C}_6\text{H}_5\text{O}'][\text{H}']}{[\text{C}_6\text{H}_5\text{OH}]}$ is only 1.3×10^{-10}

which means that only an extremely small quantity of $\text{C}_6\text{H}_5\text{O}'$ ions can exist in presence of H^+ without continuing to give undissociated $\text{C}_6\text{H}_5\text{OH}$. As a matter of fact, in the above case of sodium phenate solution, which “momentarily” gives rise to almost normal concentration of $\text{C}_6\text{H}_5\text{O}'$ ions the concentration of H^+ from the solvent is too great to allow these ions to remain uncombined with one another—since they must conform to the equation giving 1.3×10^{-10} as the dissociation constant of the acid. What happens is

that undissociated C_6H_5OH is formed, thereby using up H^+ and $C_6H_5O^-$ simultaneously, until the expression—

$$\frac{[H^+] \times [C_6H_5O^-]}{[C_6H_5OH]}$$

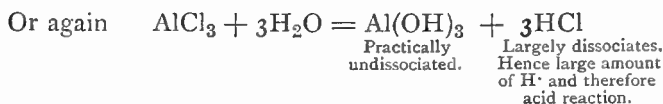
has attained the necessary value. But the disappearance of H^+ necessarily means the further production of OH^- ions from the water, since the product of $[H^+][OH^-]$ is constant, and hence the solution as a whole reacts *alkaline*—alkalinity being due to excess OH^- . This is the mechanism based on the theory of electrolytic dissociation to account for the alkalinity of solutions of sodium phenate. The same behaviour is exhibited by sodium carbonate or KCN solutions, because CO_2 and HCN are extremely weak acids. In the case in which we deal with a solution of a salt containing a weak base—say, aniline hydrochloride, or $AlCl_3$ —the resultant reaction is acid, for here the OH^- of the water is used up in combining with the Al^{+++} ions to give some undissociated $Al(OH)_3$, which is so weak a base, *i.e.* possesses so small a dissociation constant, that the product of the Al^{+++} ions and OH^- ions in the present case would exceed the necessary value for equilibrium, and since $[H^+] \times [OH^-]$ is always constant, it follows that more H^+ is produced from the water, as OH^- is used up to form $Al(OH)_3$, and H^+ remains in the solution as such, thereby giving the acid reaction. A very interesting case now presents itself, *viz.* a solution of a salt made up of two extremely weak components, *e.g.* aluminium acetate, aniline acetate, or ammonium acetate. In this case H^+ ion is removed from the solution along with acetanion to give some undissociated CH_3COOH . Simultaneously OH^- is removed from the solution along with NH_4^+ or Al^{+++} , to give undissociated NH_4OH or $Al(OH)_3$, and therefore, although the extent of the hydrolysis is very great, the solution is not so acid or so alkaline as in the previous cases. In fact, *if the dissociation constants of the acid and the base were identical, we would have hydrolysis, and yet the solution would be neutral.* The student must therefore be on his guard against assuming that absence of neutrality means absence of hydrolysis. This case, however, is extremely rare ;

and whenever acidity or alkalinity exhibits itself in a solution of a salt we can infer hydrolysis.

The simplest manner of representing a hydrolytic reaction is as follows :—

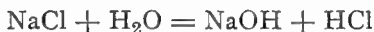


There is here excess OH' and hence the solution reacts alkaline.



In this particular case, however, it is probable that we have progressive hydrolysis (Denham, *Trans. Chem. Soc.*, **93**, 42, 1908).

The mechanism of the reaction, however, in all cases involves the ions of water rather than the undissociated molecules of water. The above method of writing the reaction is convenient, however. It will be seen that the essential thing about hydrolysis is the formation of one or more undissociated products, and this depends on the weakness of the acid and basic constituents. In the case of NaCl solution, for example, hypothetical hydrolysis might be represented by—



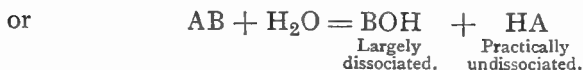
but BOTH the acid and base are practically completely dissociated, *i.e.* there is a large and equal quantity of H' and OH', and the product is much greater than K_w , and hence there is a combination of these ions, leaving the solution neutral, and no undissociated acid or base exists. The reaction may be represented in the ordinary way—



We now turn to the question—

How does the extent of the hydrolysis vary with the dilution of the system?

CASE I.—Let us take the case of a salt consisting of a *strong acid* and *weak base* or *vice versa*. The reaction is either



At equilibrium applying the law of mass action, we obtain—

$$\frac{[BOH] \times [HA]}{[AB] \times [H_2O]} = \text{constant}$$

and since $[H_2O]$ is constant,

$$\frac{[BOH] \times [HA]}{[AB]} = \text{a constant called the } \textit{hydrolytic constant}.$$

Suppose we have dissolved 1 mole of salt AB in v liters of water and x is the fraction hydrolysed, then—

$$\frac{x^2}{v^2} \cdot \frac{v}{1-x} \quad \text{or} \quad \frac{x^2}{(1-x)v} = \text{constant}$$

so that as v increases so must x , i.e. *the hydrolysis increases with the dilution*.¹ When the hydrolysis is small $1-x=1$ approximately, and x is then $\propto \sqrt{\text{dilution}}$.

ILLUSTRATION.—HYDROLYSIS OF POTASSIUM CYANIDE, KCN
(Shields, 1893).

Concentration of KCN in moles per liter = $\frac{1}{v}$.	Fraction of each mole of KCN hydrolysed, i.e. concentration of HCN (which is practically undissociated).	$\frac{x^2}{(1-x)v}$.
0.947	0.0031 or 0.31 per cent.	0.9×10^{-5}
0.235	0.0072 or 0.72 „	1.22×10^{-5}
0.095	0.0112 or 1.12 „	1.16×10^{-5}
0.024	0.0234 or 2.34 „	1.3×10^{-5}
		Mean 1.1×10^{-5}

¹ It must be observed that this is not always true (see Case II.). The only sound treatment is to consider the effect from the standpoint of ions.

We may look at the question from a somewhat different standpoint involving the ions of water rather than the undissociated molecules. Let us take as a specific case the hydrolysis of KCN.

If we start with 1 mole of KCN in v liters we find at equilibrium the concentration terms are as follows:—

$$\frac{x}{v} \text{ moles per liter HCN} + \frac{x}{v} \text{ KOH} + \left(\frac{1-x}{v}\right) \text{ KCN}$$

Neglecting the dissociation of HCN (especially in presence of CN' ions from the completely dissociated KCN, CN' concentration = $\frac{(1-x)}{v}$), we may put the concentration of *undissociated* HCN as $\frac{x}{v}$.

From the ionic product of water we have

$$K_w = [\text{H}'][\text{OH}'] \quad \text{or} \quad [\text{H}'] = \frac{K_w}{[\text{OH}']} = \frac{K_w}{\frac{x}{v}}$$

because the KOH present is completely dissociated, and this is the main source of the OH' ions.

Further writing the dissociation constant of the acid as k_a

we find
$$k_a = \frac{[\text{H}'][\text{CN}']}{[\text{HCN}]} = K_w \frac{(1-x)}{x^2 v}$$

Hence
$$\frac{K_w}{k_a} = \frac{x^2}{(1-x)v}$$

Denoting the hydrolytic constant by $\frac{x^2}{(1-x)v}$, it follows that the hydrolytic constant = $\frac{K_w}{k_a}$.

It will thus be seen that the hydrolytic constant is greater, the smaller is k_a , *i.e.* the weaker the acid. For HCN $k_a = 1.3 \times 10^{-9}$ and $k_w = 1.2 \times 10^{-14}$.

Solving for x in the above equation, we get

$$x = \frac{-vK_w}{2k_a} \pm \sqrt{\frac{v^2(K_w)^2}{4} + \frac{vK_w}{k_a}}$$

In the cases in which $\frac{K_w}{k_a}$ is small compared with unity, *i.e.* when k_a is considerably larger than K_w , the expression reduces to

$$x = \sqrt{\frac{vK_w}{k_a}} \quad \text{i.e. } x \propto \sqrt{v} \text{ as before}$$

The hydrolysis of a salt consisting of *one* weak constituent can be calculated if we know the ionic product of water and the dissociation constant of the weak constituent.

CASE II.—Now consider the hydrolysis of a salt containing *both* a weak acid and weak base, *e.g.* urea acetate or aniline acetate. If we start with 1 mole of the salt in v liters, and a fraction x is hydrolysed, then the equilibrium corresponds to $\frac{1-x}{v}$ moles of salt practically completely dissociated,

$$\text{i.e. } \frac{1-x}{v} = \text{the concentration of } A' \text{ or } B'$$

likewise there are $\frac{x}{v}$ moles acid very slightly dissociated

and $\frac{x}{v}$ „ base „ „

We must take into account the dissociation constants k_a and k_b of the free acid and base. From the dissociation of water we have the relationship

$$[H^+][OH'] = K_w$$

For the acid
$$\frac{[H^+][A']}{[HA]} = k_a$$

For the base
$$\frac{[B'][OH']}{[BOH]} = k_b$$

Since the dissociation of the acid and base is very small, we may put the concentration of the undissociated acid, *viz.*

$$[HA] = \frac{x}{v}, \text{ and similarly, } [BOH] = \frac{x}{v}$$

Hence
$$k_a = \frac{[H^+] \left[\frac{1-x}{v} \right]}{\frac{x}{v}}$$

and
$$k_b = \frac{[\text{OH}'] \left[\frac{1-x}{v} \right]}{\frac{x}{v}}$$

whence $k_a \times k_b = [\text{H}'] [\text{OH}'] \left[\frac{1-x}{x} \right]^2 = K_w \left[\frac{1-x}{x} \right]^2$

In other words, $\frac{\text{concentration of acid} \times \text{concentration of base}}{(\text{concentration of unhydrolysed salt})^2}$

which is expressed by $\frac{x^2}{(1-x)^2}$, is a constant, namely $= \frac{K_w}{k_a k_b}$.

In such a case, therefore, when both constituents of the salt are weak the v term vanishes. That is to say, *the extent of the hydrolysis is independent of the dilution*. This behaviour is essentially different from that of the previous case, in which it was shown that x is proportional to v . The above conclusion was verified by Arrhenius and Walker in 1890 in the case of aniline acetate ("anilinium" acetate, compare Denham, *l.c.*).

$v =$	12.5	25	50	100	200	400	800	
$100x =$	54.6	55.8	56.4	55.1	55.6	55.4	56.9	Mean 55.7.

It has been recently pointed out by Tizard (*Trans. Chem. Soc.*, 97, 2477, 1910) that the concentration of H' ion and therefore of OH' ion in a solution of a salt (made up of two *weak* constituents) is constant whatever the dilution may be. This is seen to be a necessary deduction from the equations given, for

$$k_a = \frac{[\text{H}'] \left[\frac{1-x}{v} \right]}{\frac{x}{v}}$$

or
$$[\text{H}'] = k_a \frac{x}{1-x} = k_a \sqrt{\frac{K_w}{k_a k_b}} = \text{a constant}$$

Experimental evidence in favour of this is put forward by Tizard, based upon colorimetric measurements. The addition

of a few drops of aniline acetate solution to a neutral solution of methyl orange causes the same rise in colour as the addition of a large quantity of aniline acetate.

METHODS OF DETERMINING HYDROLYSIS AND THE HYDROLYTIC CONSTANT.

It might be thought that this would be a very easy matter, simply involving a titration of the excess H^+ or OH' , but this is quite out of the question, for if we commence to neutralise, say the free acid in the case of aniline hydrochloride, the equilibrium is disturbed and new equilibrium states are successively set up. This goes on until the whole of the HCl is neutralised. A solution of aniline hydrochloride, therefore, behaves towards alkali exactly like a solution of HCl of the same equivalent concentration. Exactly the same thing happens, say, in the case of Na_2CO_3 solution, which reacts alkaline owing to the free OH' . This cannot be titrated with acid, as otherwise the neutrality end point is only reached (using methyl orange as indicator), when the whole of the carbonate has disappeared as such, *i.e.* the solution behaves like an $NaOH$ solution of the same equivalent concentration. It is evident that recourse must be had to some method of investigation which permits us to measure the hydrolytically produced H^+ or OH' without altering the equilibrium. The methods employed are essentially physical. The most important are—

(1) Measurement of the catalytic effect of the H^+ or OH' determined by the rate of inversion of sugar, decomposition of diazoacetic ester, hydrolysis of methyl acetate, or other catalysable reaction.

(2) Electrical conductivity measurements.

(3) Determination of the lowering of freezing point.

(4) Distribution of one of the products of hydrolysis of the partially hydrolysed salt between two solvents. (3) and especially (4) are typical instances of heterogeneous equilibrium, and will be considered later on.

(5) From electrometric measurements, *i.e.* measurement of the E.M.F. of cells fitted with hydrogen electrodes. From the values obtained one can determine the concentration of the H^+ ion in a partially hydrolysed solution, and hence the extent of the hydrolysis. This will be taken up in the section on electrochemistry (Vol. II., Chap. VII.).

(6) Indirect methods: calculation of the hydrolytic constant from known values of K_w , k_a , k_b .

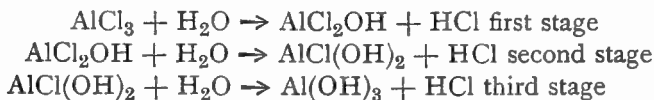
At present we shall only briefly discuss methods (1), (2), and (6).

(1) *Method based upon the inversion of Cane Sugar.*—H. Ley (*Zeitsch. physik. Chem.*, **30**, 222, 1899), employing this catalytic method, obtained the following values for the hydrolysis of $AlCl_3$, assuming a "first-stage" hydrolysis only, *i.e.* $AlCl_3 + H_2O \rightarrow AlCl_2OH + HCl$. Temperature $99.7^\circ C$. :—

v (liters) containing one equivalent of salt.	Velocity constant k .	per cent. hydrolysis = $100x$.	Hydrolytic constant = $\frac{x^2}{(1-x)v}$.
32	0.0422	8.04	2.2×10^{-4}
64	0.0346	13.2	3.14×10^{-4}
128	0.0258	19.7	3.78×10^{-4}
256	0.0185	28.2	4.33×10^{-4}
512	0.0136	41.4	5.71×10^{-4}

Ley knew by experiments with acid present alone what concentration of H^+ ions corresponded to a certain velocity constant (k). Hence by simple proportion he was able to calculate the quantity of H^+ ion which must have been present in the various salt solutions by observing the rate of inversion in the presence of these salts. Knowing the $[H^+ \text{ ion}]$ we get the quantity of salt which must have undergone hydrolysis in order to produce this H^+ ion. The source of error in the method is that the neutral salts themselves have probably a catalytic effect on the rate of inversion of the sugar, though to a much smaller extent than the H^+ ion. It will be observed that the hydrolytic constant is not very constant, rising steadily as dilution increases. This may be ascribed to a

second or even third stage hydrolysis coming in, in the above case, viz.—



Ley carried out a similar series of experiments with many other metallic salts.

The determination of hydrolysis of salts by means of the catalytic saponification of the methyl acetate by means of H^+ ions follows exactly the same general principle as the above. One may also mention the extremely delicate catalytic reaction, viz. the decomposition of diazoacetic ester by means of H^+ ions (Bredig and Fraenkel, *Zeitsch. Elektrochem.*, 11, 525, 1905) whereby $[\text{H}^+]$ down to $\frac{N}{1000}$ are determinable, but the presence of neutral salts has a disturbing effect.

The following table (taken from a report by R. C. Farmer, *British Association Report*, 240, 1901) contains the values of the percentage hydrolysis of certain salts at decinormal concentration at 25°C .:—

TABLE.

HYDROLYSIS OF HYDROCHLORIDES OF WEAK BASES as measured by the catalytic decomposition of esters.

Base.	% Hydrolysis.	Base.	% Hydrolysis.
Glycocoll . . .	19	Urea	90
Asparagine . . .	25	Acetamide . . .	98
Acetoxime . . .	36	Thiourea . . .	99

HYDROLYSIS OF ALKALI SALTS OF WEAK ACIDS as measured by the catalytic saponification of esters.

Acid.	% Hydrolysis.	Acid.	% Hydrolysis.
Hydrocyanic . . .	1.12	p. chlorophenol .	1.62
Acetic	0.008	p. cyanphenol .	0.29
Carbonic	3.17	p. nitrophenol .	0.16
Phenol	3.05		

HYDROLYSIS OF HYDROCHLORIDES OF WEAK ORGANIC BASES measured by the rate of inversion of cane sugar.

Base.	% Hydrolysis.	Base.	% Hydrolysis.
Pyridine . . .	1·2	Urea	81
Quinoline . . .	1·2	Acetamide . .	78
Aniline	2·6	Asparagine . .	21

HYDROLYSIS OF THE CHLORIDES OF CERTAIN METALS as measured by the rate of inversion of cane sugar.

Base.	% Hydrolysis.	Base.	% Hydrolysis.
Zinc	0·1 at 100° C.	Aluminium . . .	2·7 at 77° C.
Lead	0·2 " "	Cerium	0·3 at 100° C.
Beryllium . . .	1·8 " "	Lanthanum . . .	0·1 " "
Aluminium . . .	6·1 " "	Iron (Ferric) . .	10 at 40° C.

(2) *The Conductivity Method.*—If a salt—say, aniline hydrochloride—is hydrolysed to the extent x , then for a solution the total concentration of which is known and the specific conductivity is observed, the following relation holds, viz.:—

$$\Lambda = (1 - x)\Lambda_v + x\Lambda_{\text{HCl}}$$

where Λ stands for the apparent equivalent conductivity, *i.e.* the product of the *observed* specific conductivity into the volume containing one equivalent of the salt. The hydrochloric acid may be regarded as completely dissociated, and its conductivity is therefore constant. Such a solution does not obey Kohlrausch's Law for the mobilities of the ions. (In the above expression we have neglected the conductivity due to the practically undissociated base or basic salt formed by hydrolysis.) Solving for x in the above equation, one obtains—

$$x = \frac{\Lambda - \Lambda_v}{\Lambda_{\text{HCl}} - \Lambda_v}$$

We can set Λ_{HCl} , the equivalent conductivity of HCl, at

infinite dilution,¹ as equal to 383 at 25°. Λ_v stands for the equivalent conductivity the salt *would* have possessed had no hydrolysis taken place.

This can be evaluated by the method of Bredig (*Zeitsch. physik. Chem.*, 13, 214, 1894), namely, by the addition of a sufficiently great excess of the free base to the hydrolytic salt solution until we reach the condition that—

$$\Lambda = \Lambda_v, \text{ i.e. } x = 0$$

which must be obtained when the Λ *observed* has become independent of the quantity of free base added. The applicability of this method obviously depends on the validity of assuming that the conductivity of the base itself is negligibly small compared with that of the salt. The following data are given by Bredig (*l.c.*) for the hydrolysis of aniline hydrochloride:—

The column headed Λ denotes the values of the equivalent conductivity when the solution is diluted with water only.

The column marked $\Lambda_v(32)$ denotes equivalent conductivity with $\frac{N}{32}$ aniline present in the solution.

The column marked $\Lambda_v 64$ denotes values obtained with $\frac{N}{64}$ aniline present.

..	Λ .	$\Lambda_v(32)$.	$\Lambda_v 64$.
64	106.2	95.9	96.0
128	113.7	98.1	98.2
256	122.0	100.1	100.3
512	131.8	101.4	101.5
1024	144.0	103.3	103.3

The agreement between the two final columns shows that even with $\frac{N}{64}$ aniline present the hydrolysis of the salt has practically disappeared, for on increasing the aniline to

¹ Strictly the HCl will not be in general completely dissociated, but no very serious numerical error is thereby introduced.

$\frac{N}{32}$ the same value for Λ_v is obtained; the Λ_v in both cases being due simply to the two ions $C_6H_5NH_3^+$ and Cl^- .

By such means we obtain the value of Λ_v , *i.e.* the true equivalent conductivity of the unhydrolysed salt at dilution v , whilst the observed equivalent conductivity at the same dilution when hydrolysis actually occurs is given by Λ . The equation can thus be solved. The following data are given by Bredig (*l.c.*, p. 322) for the hydrolysis of aniline hydrochloride at 25° C. :—

v .	Λ .	Λ_v .	% Hydrolysis = $100 x$.	$\frac{k_a}{k_w} = \frac{1}{K}$ (hydrolytic constant).
32	99.6	92.1	2.63	45×10^3
64	106.2	95.1	3.90	40×10^3
128	113.7	98.1	5.47	40×10^3
256	122.0	100.1	7.68	40×10^3
512	131.8	102.1	10.4	42×10^3
1024	144.0	103.1	14.4	42×10^3
				Mean 41×10^3

In the case of stronger bases than aniline their conductivity could not be neglected compared with Λ_v when v was large, *i.e.* at concentrations of base such as $\frac{N}{32}$ or $\frac{N}{64}$. In such cases more dilute solutions of the base have to be employed, for although the degree of dissociation of the base is greater the greater the dilution, the less is the absolute concentration of ions, and hence the less the effect upon the conductivity of the mixed salt and base.¹ It has been pointed out by Farmer (*Brit. Assoc. Report*, p. 240, 1901) that the conductivity method on the whole is not particularly accurate.

The Indirect Method (6).—We have already considered the

¹ The conductivity method in a modified form differing from that described has been employed by Walker (*Zeitsch. physik. Chem.*, **4**, 333, 1889) to measure the hydrolysis of chlorides and sulphates of weak bases,

methods of obtaining k_a and k_b the dissociation constants of acid and base respectively. The determination of K_w , the ionisation constant for water, will be taken up later. Indeed, the degree of hydrolysis—measured by some one of the direct methods—has been employed as one of the means of calculating K_w . The values obtained by the direct methods (1 to 5) of determination of the hydrolysis, and therefore the hydrolytic constant yield values of K_w , which are in good agreement with those determined directly; and such agreement must necessarily be regarded as one of the most convincing pieces of evidence in favour of the theory of electrolytic dissociation.

THEORY OF INDICATORS.

An indicator is an electrolyte—essentially a weak acid or weak base—which gives rise to a colour change according as the solution into which it is introduced is made acid or alkaline. The action on the basis of the dissociation theory depends on the alteration produced in the degree of the dissociation of the indicator according to the amount of H^+ or OH^- present in the solution. The effectiveness depends on the property of a colour change accompanying the change in dissociation, that is, the undissociated molecule must possess a colour which differs from that of its ions, and the more marked the contrast is, the better, *ceteris paribus*, is the indicator. Since it is known that H^+ and OH^- themselves have no colour, an indicator which is a base, *i.e.* a basic indicator, must possess a coloured cation; an acid indicator must possess a coloured anion. The undissociated molecule must be either colourless, or differ in colour from the ion. The weakness of the indicator is essential, since the weaker it is the more will its dissociation depend on the variation of the H^+ or OH^- in the solution during the process of titration, and hence the sharper will the end point be. Very marked weakness alone, however, is not the deciding factor, as this in itself brings in certain effects, such as hydrolysis, to which reference will be made. As a typical acid

indicator we may take phenolphthaleïn. This acid is extremely weak. The undissociated molecule is colourless. When completely dissociated, say, in the form of its sodium salt, the solution is bright pink, which must be due to the anion, since Na^+ has no colour effect in the visible spectrum. In acid solution, *i.e.* in presence of relatively small H^+ concentration, the dissociation of phenolphthaleïn will be thrown back so as to be practically undissociated, and hence the solution is colourless. In alkaline solution—excess of OH' —the H^+ produced by the indicator acid will unite with OH' to give H_2O , and this process goes on until dissociation of the indicator is practically complete, and hence the solution is brightly coloured. Since the indicator is weak, a small drop of titrating acid or alkali will cause a sufficient change in the relative H^+ and OH' concentration to cause the above marked colour change. Again, take methyl orange, an acid which is weak, but not nearly so weak as is phenolphthaleïn. The undissociated molecule is red, the cation is yellow. In acid solution, *i.e.* in presence of H^+ in excess, the indicator dissociates a little more than phenolphthaleïn but still practically not at all, and the solution is red in colour. In alkaline solution, *i.e.* excess OH' , the dissociation of the indicator takes place, and the solution is yellow.

The problem may be looked at from the standpoint of relative avidity which we have considered. Suppose we start with a colourless solution containing some phenolphthaleïn in presence of the acid we desire to titrate. Caustic soda is added from the burette and distributes itself between the two acids present. We have seen that this distribution takes place (when the two acids are present in equivalent proportions) in the ratio of the square roots of their dissociation constants. Hence the advantage of phenolphthaleïn being very weak—it only gets a very small fraction of the base, and this inequality is still further increased by the fact that the concentration of the indicator is extremely small compared with that of the acid which is being titrated. If the indicator takes up the alkali, it of course dissociates, being now a salt, and the colour begins to appear. This, however, will be deferred until practically

all the other acid has been titrated, *i.e.* converted into salt, and the production of colour, which must theoretically be a gradual process, only makes itself apparent within the limits of a small drop of alkali, *i.e.* within the limits of the accuracy of the titration. Exactly similar reasoning holds good in the case of methyl orange. Since phenolphthaleïn is the weakest acid indicator known, it is specially suitable for the titration of weak acids. It must be noted, however, when the indicator is phenolphthaleïn, that it is preferable to use a *strong* alkali as titrating agent, such as KOH or NaOH, not NH_4OH , so as to prevent hydrolysis, because the hydrolysis of a salt formed from a weak acid and weak base is much greater than that of a salt containing one strong component. Thus, suppose we had an acid solution, say, HCl, containing a little phenolphthaleïn, and were titrating it with ammonia, NH_4Cl (dissociated) is produced in large quantity, thereby driving back the dissociation of the ammonia itself, and therefore reducing the OH' ions which should be free when the HCl is just neutralized. If this effect on the ammonia is marked, *i.e.* if there is much NH_4Cl present, it is quite conceivable that the OH' produced by the drop of ammonia, even when the titration is complete, is scarcely great enough to cause the indicator to dissociate. In other words, the titration is not sharp. This is the same thing as saying that the ammonium salt of the indicator acid is largely hydrolysed, for hydrolysis in this case gives rise to a weak acid (the colourless phenolphthaleïn) and a weak base (NH_4OH) in large quantity, leaving a correspondingly smaller quantity of phenolphthaleïn ion (and NH_4') present in the solution. On adding excess ammonia in the titration, therefore, the colour gradually appears, the addition of titrating agent required being now quite outside the limits of error inherent in making the determination, *i.e.* the burette reading. Hence the inaccuracy of the method. In the case of methyl orange as indicator, owing to the methyl orange being much stronger than phenolphthaleïn, the accuracy of titration is not so dependent on the strength of the titrating base.

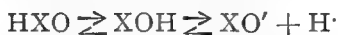
The strength of methyl orange, however, is not always an

advantage, as very weak acids cannot be titrated with it, for if the acid is, say, of comparable strength to the indicator, then on adding alkali the indicator—in spite of its smaller concentration relative to the other acid—may take a gradually increasing share of the alkali, and hence *gradually* change in colour, thereby giving no sharp end point.

From the above considerations we may deduce the following rules. If we have to titrate—

1. Strong acid and strong base—use any indicator.
2. Strong acid and weak base—indicator strongest, *e.g.* methyl orange, nitrophenol (acid).
3. Weak acid and strong base—indicator weakest, *e.g.* phenolphthaleïn, litmus.
4. Weak acid and weak base—to be avoided.

Modification of the foregoing Theory of the Sensitiveness of Indicators.—The simple theory of Ostwald, in which the colour change is ascribed directly and entirely to change in ionisation of the indicator, has been shown to be not quite correct. On the new theory, however, an indicator, say, an acid, in the undissociated form is a mixture of two or more tautomeric forms, HXO and XOH in equilibrium. Under suitable conditions the form XOH ionises, giving rise to the ions XO' and H' . The form HXO does not ionise of itself (see p. 317 *seq.*). The equilibrium equation of the whole indicator process is therefore—



Owing to similarity in structure the individuals XOH and XO' must be similarly coloured, H' is colourless, and HXO being differently constituted to the other species present, may possess any colour or none. Thus HXO may be deep red, XOH and XO' pale yellow in equivalent solutions. When the indicator is placed in an acid solution its ionisation decreases, that is, XOH increases, and this in turn gives rise to more HXO , the solution thereby turning red. On the other hand, if the solution is alkaline the dissociation of the indicator proceeds practically to completion. That is, the XOH concentration falls rapidly, and is made good at the expense of HXO , which then disappears, the solution becoming

thereby yellow. If the solution were neutral it is conceivable that a limit midway between the two might be obtained. This is the case with litmus, in which the HXO form is bright red, the ions XO' and the molecule XOH blue, the neutral solution being purple. Now ionic changes are instantaneous, the speed, therefore, with which an indicator changes its colour with changing acidity or alkalinity of the solution depends on the velocity of the tautomeric molecular change. A good indicator must possess the property of extremely rapid tautomeric change. Let us still further consider the case of an indicator which is a weak acid, its degree of dissociation being represented by α at the particular dilution investigated. Then applying Ostwald's Law we find that—

$$k_a \times \text{concentration of undissociated molecules} = C_{\text{XO}'} \times C_{\text{H}^+}$$

$$\text{or} \quad k_a \cdot \frac{1 - \alpha}{\alpha} = \text{concentration of H}^+$$

where k_a is the dissociation constant of the indicator.

The degree of ionisation of an indicator, and therefore its colour, depends on the value of k_a and the H' in the solution. Let us take a particular case. Suppose $\alpha = \frac{1}{2}$, then—

$$k_a = C_{\text{H}^+}$$

That, is when the concentration of the H' in the solution is numerically equal to the dissociation constant of the indicator, the latter is one-half ionised, and exhibits a colour midway between the two extreme colours corresponding to complete ionisation and zero ionisation respectively. Take another special case, viz.

$$C_{\text{H}^+} = 10k_a$$

Evidently here α must be 0.09 or 9 per cent. That is, the indicator is practically in the un-ionised state, and the colour will correspond to the un-ionised state. On the other hand, if $C_{\text{H}^+} = \frac{1}{10}k_a$, then $\alpha = 0.91$ or 91 per cent. The ionisation is now nearly complete, and the colour will be practically that corresponding to complete ionisation. Hence we arrive at the important conclusion that if we know the dilution of the indicator in a given solution, we can say at once within what

limits of H^+ the colour will change. That is, if we find that the indicator is showing a midway colour, we can say that the H^+ ion in the solution lies between certain maximum and minimum values. For example, we can take a series of aqueous solutions containing H^+ ion at the following concentrations: 10^{-3} , 10^{-4} , 10^{-5} , 10^{-6} , 10^{-7} (neutral point at $25^\circ C.$) 10^{-8} , 10^{-9} , etc., equivalents per liter, and add small quantities of indicator to each. If methyl orange is the indicator, it will be found to be bright red in the 10^{-3} H^+ solution, orange in the 10^{-4} H^+ , and yellow at 10^{-5} H^+ . We conclude, therefore, that its dissociation constant lies in the neighbourhood of 10^{-4} . Phenolphthalein is colourless in 10^{-7} , feebly coloured at 10^{-8} , and deeply coloured at 10^{-9} . Its dissociation constant lies, therefore, in the region of 10^{-8} .

The remaining considerations upon the subject of indicators are quoted from an article by H. T. Tizard (*British Assoc. Report*, 1911, p. 268).

"It is evident that if we wish to define with greater exactness the ranges of sensitiveness of indicators in this way we must measure as accurately as possible their dissociation constants. This, however, is by no means an easy task; an indicator is generally both too weak and too insoluble an electrolyte for us to be able to determine its dissociation constant by the ordinary conductivity method. The only accurate method appears to be a quantitative measurement of the depth of colour of the indicator in solutions of different, accurately known, concentration of hydrions. This is only convenient when the indicator is only coloured in one form or has two coloured forms which practically do not differ in tint, but only in depth of colour.¹ Approximate determinations made by means of the solutions already referred to are sufficient for most ordinary work, and it would be of the greatest assistance if in future every discoverer of a new indicator would test his product in this manner.

"Since the concentration of hydrogen ions in pure water is 10^{-7} at 25° , it follows that the exact neutral point is only indicated by an indicator with a dissociation constant of about

¹ See *Trans. Chem. Soc.*, 1910, p. 2477.

10^{-7} (litmus). It does not follow that this is the most useful indicator, in fact the contrary is true. Speaking generally, however, we may say that the most sensitive indicators are those which have dissociation constants not widely different from 10^{-7} ; for evidently the change from 10^{-3} to 10^{-5} (methyl orange), that is from one-thousandth to one-hundred-thousandth normal, is more considerable than the change from one-millionth to one-hundredth-millionth normal. An indicator must therefore be a weak acid or base, as Ostwald said. But it must not be too weak; an indicator with a dissociation constant of 10^{-11} , for example, changes over between concentrations of hydrogen ions of 10^{-10} and 10^{-12} , that is to say between concentrations of hydroxyl ions of 10^{-4} and 10^{-2} (since $C_H \times C_{OH} = 10^{-14}$ at 25°). Such a change is only brought about by addition of a considerable amount of alkali).¹

“It is now possible to apply these conclusions to the actual process of titration. If an alkaline solution be gradually added to an acid solution, the concentration of hydrogen ions in the latter become smaller and smaller until a point is reached when the indicator present begins to dissociate appreciably. This point may or may not be the point when exactly equivalent quantities of base and acid are present together; that depends obviously upon the indicator used. Now we can either stop the titration directly we observe a distinct change in colour, or when further slight addition of alkali has no more appreciable effect. In practice it has been found most convenient to take as our end-point the *last*

¹ The range of sensitiveness of an indicator probably alters considerably with the temperature. The “apparent” dissociation constants of all pseudo-acids and bases have been found to have high temperature coefficients, and indicators should form no exception to this rule. If a 200th normal solution of acetic acid ($C_H = 3 \times 10^{-4}$) containing methyl orange be warmed from 0° to 25° , the colour of the solution becomes distinctly paler, although the dissociation constant of acetic acid alters very little with the temperature, and in any case C_H does not become smaller. The phenomenon is best explained by an increase in the dissociation constant of methyl orange. It follows that when indicators are used for the colorimetric determination of hydron concentrations, care should be taken to keep the temperature constant—a precaution which has not been thought necessary up to the present.

part of the colour change when we titrate from a dark to a light colour, and the *first* part of the colour change when we titrate in the reverse direction; and it is evident that, other things being equal, those indicators will give the sharpest and most satisfactory end-point which exhibit the greatest difference in depth of colour or tint between their two forms, because it is then an easy matter to detect a very small change in ionisation. Does the end-point depend upon the amount of indicator present? In the case of two-coloured indicators, such as methyl orange and methyl red, it does not, for we always titrate to a certain *fractional* change of the indicator. With mono-coloured indicators, such as phenolphthaleïn, it is different. In this case we go on adding alkali until there is a perceptible colour in the solution—that is to say, until there is a certain *amount* of coloured substance in the solution. If there is a large quantity of indicator present, this amount may be a very small fraction of it; if a small quantity, this amount may be a large fraction, and a glance at the equation—

$$k_a \times \frac{1 - \alpha}{\alpha} = \text{concentration } H^+$$

will show that the smaller α is, the higher is the concentration of hydrogen ions indicated. A limit is, however, put on this by the insolubility of the indicator. In the particular case of phenolphthaleïn, the more indicator we use the more sensitive it is to small concentrations of hydrions, and the nearer is its “end-point” to 10^{-7} , the theoretical neutral point. Owing to its insolubility, however, it is doubtful whether it can be used to indicate concentrations of hydrogen ions higher than $10^{-7.5}$.

“This influence of the amount of indicator present in the solution has not been sufficiently recognised, and may partly account for the differences in the value for the end-point of phenolphthaleïn given by different observers.

“It may be remarked that it is possible for the amount of indicator present to affect the titration in another way. It has already been said that if a two-coloured indicator is used, the titration is continued until a certain fraction of the indicator,

say about 95 per cent., is changed over into the form of ions. Now this change, or neutralisation, of the indicator does actually require a certain definite amount of alkali for its completion, and the more indicator is present the more alkali will be needed. Most indicators of this class are, however, used in such dilute solution that this effect is negligible; and it is further important to notice that even if the concentration of the indicator is moderately high, the accuracy of the titration will not be affected if the indicator is originally put into the solution in the same form as it will have at the end of the titration. From this point of view, such indicators as methyl orange, methyl red, nitrophenol, must be used in the form of their sodium or potassium salts.

“Bearing all these facts in mind it is possible to draw up a table showing the ‘end-points’ of various indicators when used in the ordinary manner in titration. Thus we have already seen that the colour change of methyl red is only complete when the concentration of hydrogen ions is something less than 10^{-6} ; and the end-point observed when methyl red is used as an indicator in the ordinary manner lies somewhere between $10^{-5.7}$ and $10^{-6.4}$, the variation being relatively unimportant, and due to the inability of the eye to detect small changes in colour without a special apparatus. The following table gives the values of the end-points of the more common indicators; the actual numbers are probably not extremely accurate in some cases, but our knowledge is at present too imperfect to allow of their being defined with greater precision:—

Methyl orange	$10^{-4.5}$ to $10^{-5.5}$
Methyl red.	$10^{-5.7}$ to $10^{-6.4}$
Litmus	$10^{-6.5}$ to $10^{-7.5}$
Phenolphthaleïn	$10^{-8.2}$ to 10^{-9}
Thymolphthaleïn	$10^{-10.5}$ to $10^{-11.5}$

“Having arrived at these numbers, all that remains is to consider how the concentration of hydrogen ions changes in a solution when we titrate acids and bases of various strengths. When we know this, we can not only decide upon the

best indicator to use, but also estimate the probable error in using it, and the absolutely certain error in using any different one. If the acid and base used are both 'strong' electrolytes, for example, HCl and NaOH, then when equivalent quantities are present in solution we have an exactly neutral solution of an unhydrolysed salt (NaCl), and the concentration of hydrions will be exactly the same as in pure water, namely 10^{-7} at 25° . Also, a very slight excess of acid and base makes an enormous difference in the concentration of hydrions in the solution. This can be seen most clearly by the accompanying curve, which represents the change in H^+ ion concentration when the titration of 50 c.c.

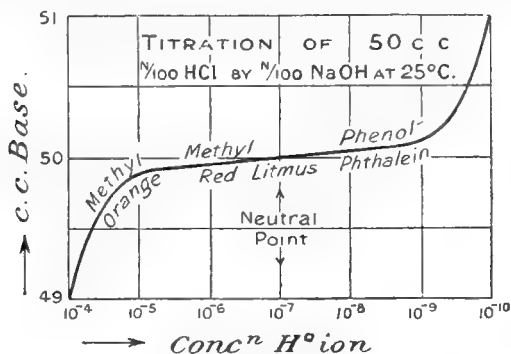


FIG. 29.

N/100 HCl by N/100 NaOH is almost complete. As ordinates are plotted the number of c.c. of base added; the abscissæ represent the concentration of H^+ ions. When 49.95 c.c. of base are added the concentration of hydrions is 10^{-6} ; when 50.05 are present, C_{H^+} is 10^{-8} ; thus two drops of the alkali, or two parts in 1000 present, diminish C_{H^+} to 100th part. Along the curve are written in the various indicators at points which correspond to the 'end-points' they indicate. It will be seen that methyl red, litmus, phenolphthalein, coming as they do on the flat, or most sensitive part of the curve, all give sharp end-points, by which we mean that a small trace of the titrating solution is enough to make a sharp change in the colour. For methyl red about a drop of alkali is enough to

decide its end-point; but the result so obtained (49.95 c.c.) may differ by about 1 part in 1000 from the true value. Phenolphthalein gives an equally sharp end-point, the error of which is a little over 1 part in 1000 in the other direction. We could therefore titrate with both in the solution, and take as the most correct result the mean of the two values obtained. For most purposes, however, an accuracy of 1 part in 1000 is ample. Methyl orange, however, comes on the steep part of the curve, and its colour changes comparatively slowly. Also the final result, which will be about 49.8 c.c., is considerably less accurate than those given by the other indicators used. Litmus should give the exact point; many workers find it,

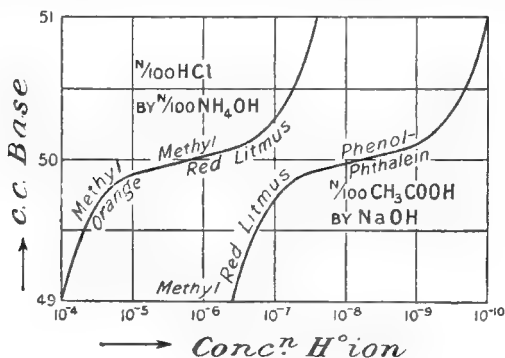


FIG. 30.

however, an inconvenient indicator to use; perhaps if its constitution could be determined, and a pure product prepared, it would again come into extensive use.

"Still more striking is the difference between the results obtained by using various indicators when one of the titrating liquids is a weak electrolyte. In this case, as is well known, the concentration of H^+ ions in the solution when exact equivalents of acid and base are present is not the same as in pure water, owing to the hydrolysis of the salt, or, in other words, incomplete combination of the acid and base. Further, excess of acid or base does not alter the concentration of H^+ ions to a large extent, since it is partly used up in destroying hydrolysis; also, if the weak electrolyte is in

excess, the degree of its dissociation, small in any case, is further reduced by the presence of the neutral salt. Even in the titration of ammonia by HCl, and acetic acid by soda, where hydrolysis is as a matter of fact extremely small, and easily destroyed altogether by a slight excess of either constituent, we find that the flat part of the curve is much narrower and much less flat. Instead of there being a number of indicators which would give accurate results, we find only methyl red in one case, and phenolphthaleïn in the other. Methyl red gives not only an accurate but a sharp end-point in ammonia titrations; phenolphthaleïn, instead of also giving an accurate result, gives an extremely inaccurate one, certainly not within 2 or 3 per cent. Methyl orange gives a better result in this case than phenolphthaleïn, but still not a sharp end-point. These facts have of course been long known, but the curves show well the magnitude of the errors involved—an important factor. In the titration of acetic acid by soda, methyl red gives an inaccurate and extremely bad end-point, phenolphthaleïn a sharp and accurate one. If the base or acid used is still weaker, it becomes very difficult to find a good indicator, and finally impossible; the flat part of the curve in fact tends to disappear until at last it does so altogether. As an example we can take *aniline*. Here, owing to the great hydrolysis of aniline hydrochloride in solution, the concentration of hydrions at the 'equivalent' point is as high as $10^{-3.5}$ and a large excess of acid or base produces only a slight change in this value. Since such concentrations of H^+ ions *do* actually affect the colour of methyl orange appreciably, it might be possible to titrate aniline to about one per cent. by using a comparison solution and a colorimeter, but evidently it is quite impossible to find an indicator capable of giving even moderately accurate results without this means.¹

¹ The concentration of hydrogen ions at the (true) end-point of a titration alters of course with the temperature, being in general about three times as small at 0° as it is at 25°. Reference to the curves given will show that this difference has very little effect on the probable accuracy of the titration, except when the acid or base titrated is extremely weak. It must be remembered that the effect is considerably lessened by a simultaneous decrease in the dissociation constant of the indicator.

"A curve showing the titration of ammonia by acetic acid is also given : it will be seen that even though the concentration of hydrions at the 'equivalent' point is 10^{-7} , the curve is very nearly a straight line, and litmus is the only indicator that might possibly give moderately accurate results. But as it is never necessary to titrate a weak acid by a weak base, it is unnecessary to discuss this and similar cases further.

"The general conclusions to be drawn from the curves are these : firstly, that if we can find an indicator which will give a sharp and satisfactory 'end-point' in any particular volumetric operation, then the end-point so indicated will probably

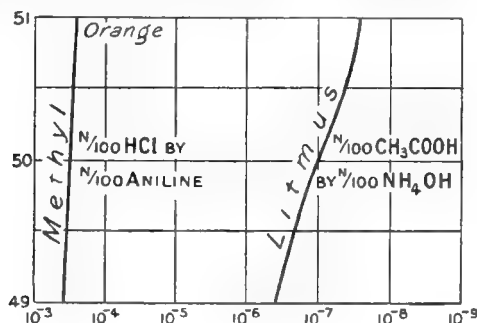
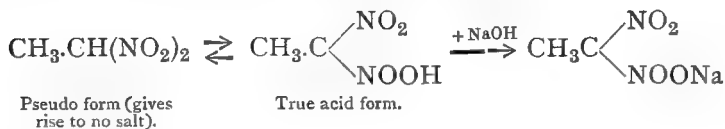


FIG. 31.

be accurate to within two parts in a thousand ; secondly, that if no indicator will give a satisfactory end-point, then the only way to obtain really accurate results is to find an indicator the colour of which is sensibly affected at the concentration of hydrions obtaining in a pure solution of the salt of the strong and weak electrolytes, and then, using a comparison solution of the salt containing the same amount of indicator as the titrating solution, titrate to the same colour. In extreme cases results obtained by judging the colours with the unassisted eye will be too inaccurate, and a form of colorimeter should be used."

PSEUDO-ACIDS AND PSEUDO-BASES.

From the theoretical consideration of hydrolysis already given it will be evident that the possibility exists of calculating the strengths (*i.e.* the dissociation constants) of acids and bases the electrical conductivity of which may be too small to be determined directly in an accurate manner. This, however, depends essentially on the assumption that no intramolecular rearrangement takes place when the salts are formed. In certain cases, however, notably certain dyestuffs, indicators, etc., such changes do take place, *i.e.* the constitution of the salt is essentially different from the constitution of the acid. This is accompanied by several characteristic anomalies in behaviour. For example, Hantsch found that such (sodium) salts, though formed from extremely weak acids, showed only *slight* hydrolysis. In the case of dinitroethane Hantsch observed that both the acid itself and the Na salt were neutral, yet the possibility of an acidic form for dinitroethane is manifestly shown by the existence of a sodium salt; and further this might be expected to be very largely hydrolysed. Hantsch accounted for such behaviour by assuming the existence of a pseudo-acid form (the ordinary substance) which could change into a true acid form, and hence be capable of giving rise to a sodium salt. Since such a change is not necessarily instantaneous, the process of neutralisation by the alkali may—and is in many cases—a slow one. In the case of dinitroethane it may be assumed that we are dealing with the following series of changes—



The following are examples of pseudo-acids and bases:—nitroparaffins, nitro acetone, alkylnitrolic acids, oxythiazoles, cyanacetic amide, nitrosamines, oxyazo compounds, pyrazolones, oximes, oxamido ketones, nitrophenols.

The characteristics of pseudo bodies are :—

- (1) Slow neutralisation (not present in all cases, however).
- (2) Abnormally slight hydrolysis.
- (3) No salt formation with NH_3 (or only very retarded formation) in benzene solution or any non-dissociating solvent.
- (4) Salts coloured ; acid or base colourless or nearly so.
- (5) Abnormal temperature coefficient of conductivity of the salt.
- (6) Abnormal conductivity in aqueous-alcoholic or alcoholic solution, *i.e.* the conductivity is decreased in this solvent much more than in the case of true acids or true bases.

Hantsch's theory is that we are dealing with tautomeric forms as in the case of dinitroethane. That this theory is not comprehensive enough is shown by the fact that it offers no explanation of the characteristic slight hydrolysis frequently noticed ; for from the nature of the substance—even the tautomeric true acid or base—it is evident that we are dealing with weak bodies, and hence the salts formed from them should be extensively hydrolysed, which is not the case. For further information upon the subject of pseudo-acids and pseudo-bodies generally the reader should consult the *Annual Reports* issued by the Chemical Society during the last few years. For a purely dynamical view of pseudo-acids and bases which does not involve special "static" formulæ for the various coloured bodies obtained, the reader is referred to a paper by E. C. C. Baly, *Trans. Chem. Soc.*, 1915, p. 248.

AMPHOTERIC ELECTROLYTES.

Ostwald observed that the dissociation constant of amino-acids varied with the dilution. Wislicenus tried to explain it by polymerisation, but this was later shown to be incorrect. J. Walker, from 1904 onwards (*Proc. Roy. Soc.*, vols. 73 and 74, 1904, and later volumes), was the first to investigate the matter thoroughly.

Consider an ordinary acid in solution. The ions present are—

$\text{H}^+ \quad \text{OH}^- \quad \text{X}^- \quad \text{XH}$ undissociated.

The equilibrium concen- }
trations being } $a \quad b \quad c \quad u$ respectively.

Then $ab = K_w$, where K_w is the ionisation constant of water.

$ac = k_a u$, where k_a is the Ostwald constant for the acid.

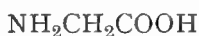
Also $a = b + c$ for electric neutrality

$$\therefore a^2 = K_w + k_a u$$

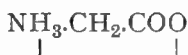
and neglecting K —

$$a^2 = k_a u \text{ the ordinary Ostwald dilution expression.}$$

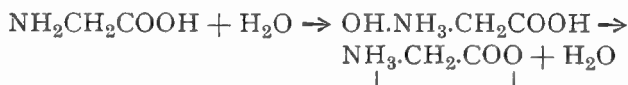
Now take the simplest type of amino-acid, namely, glycollic acid, the formula of which is—



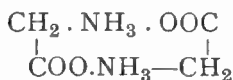
This can give rise to an internal salt—



which naturally suggests the mechanism—



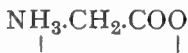
It is also possible that external salt formation might take place between two molecules, viz.—



That this, however, does not take place is shown by the fact that a molecular weight determination by the ordinary method leads to a normal value.

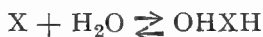
The unionised substances in solution are, therefore, the greater part of $\text{NH}_2\text{.CH}_2\text{.COOH}$ in equilibrium with its ions,

and



and also a hydrated form, $\text{OH.NH}_3\text{.CH}_2\text{.COOH}$, which might be written in general OH.X.H .

Since this salt is formed by addition of water—



in dilute solution, we can put—

$$[X] = k[OHXH]$$

or
$$\frac{[X]}{[OHXH]} = k,$$

since the concentration of the water is regarded as constant.

Besides OHXH in the unionised form, we have likewise ions produced from it, and this production can take place in two ways, viz.—

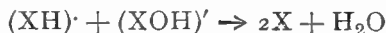
an acid dissociation,



and a basic dissociation,



There is also conceivably a reaction between the ions to give a salt, viz.—



The total ions in solution are therefore—

	H'	OH'	XOH'	XH'	HXOH	X
at the respective concentrations}	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>

These quantities are connected by the following equations :

(1) $ab = K_w$ (ionisation constant of water)

(2) $bd = k'_b e$ (k'_b is the Ostwald constant of substance, HXOH acting as a base, *i.e.* "basic dissociation")

(3) $ac = k'_a e$ (k'_a is the Ostwald constant of HXOH acting as an acid, *i.e.* "acid dissociation")

(4) $cd = Qf^2$ from "salt formation" equation

(5) $a + d = b + c$ for electrical neutrality of the solution as a whole.

Hence $abcd = k'_a k'_b e^2$ from (2) and (3).

also $abcd = KQf^2$ from (1) and (4).

$$\therefore KQf^2 = k'_a k'_b e^2$$

$$\therefore \frac{e}{f} = \text{constant independent of dilution.}$$

We have already seen this as a general phenomenon of hydrate

or solvate compound formation (p. 222). It is clear that it is simply the inverted form of the previous expression—

$$\frac{[X]}{[OHXH]} = k.$$

Since $\frac{e}{f} = \text{constant at all dilutions}$

$$\frac{e+f}{e} = \text{constant at all dilutions.}$$

Setting $e+f=u$, the above equations may be rewritten—

- (1) $ab = K_w$
- (2) $bd = k'_b e = k'_b (\text{const.} \times (e+f)) = k'_b (\text{const.} \times u)$
 $= k_b u$
- (3) $ac = k_a u$
- (4) $cd = Q f^2$
- (5) $a+d = b+c$ for electric neutrality.

We will now obtain alternate expressions for a , b , c , and d .

Since $a+d = b+c$

$$a + \frac{k_b u}{b} = b + \frac{k_a u}{a}$$

$$\therefore a^2 + \frac{k_b u a}{b} = ab + k_a u$$

Now $ab = K_w$

$$\therefore a^2 + \frac{k_b a^2 u}{K} = K_w + k_a u$$

$$\text{or } a^2 \left(1 + \frac{k_b u}{K} \right) = K_w + k_a u$$

$$\text{or } a^2 = \frac{K_w + k_a u}{1 + \frac{k_b u}{K}}$$

[Note that for ordinary acids the above equation would have been $a^2 = k_a u$.]

Also, since $ab = K_w$

$$b = \frac{K_w}{a}$$

and since

$$ac = k_a u$$

$$c = \frac{k_a u}{a}$$

Further, since

$$bd = k_b u$$

$$d = \frac{k_b u}{b} = \frac{k_b u_a}{K}$$

Now consider the special case of an amphoteric electrolyte whose basic dissociation constant k_b = the acidic dissociation constant k_a .

As before—

$$ac = k_a u$$

$$bd = k_b u$$

and since

$$k_a = k_b$$

it follows that

$$ac = bd$$

$$\therefore \frac{b+c}{b} = \frac{a+d}{a}$$

Also, since the solution is electrically neutral, it follows that—

$$a + d = b + c$$

$$\therefore a = b \quad \text{i.e.} \quad [\text{H}^*] = [\text{OH}']$$

and

$$c = d \quad [\text{XOH}'] = [\text{XH}^*]$$

The solution is therefore chemically neutral at all dilutions, since

$$\text{OH}' = \text{H}^* = 10^{-7} \text{ gram-equiv. per liter.}$$

Again,

$$c = \frac{k_a u}{a} \quad d = \frac{k_b u}{b} = \frac{k_b a u}{K}$$

$$\therefore c + d = \frac{k_a u}{a} + \frac{k_a a u}{K}$$

$$\therefore \frac{c+d}{u} = k_a \left[\frac{1}{a} + \frac{a}{K_w} \right]$$

Now a has been shown to be constant at all dilutions.

Hence—

$$\frac{c+d}{u}$$

is constant at all dilutions, *i.e.* the degree of dissociation of the amphoteric body is independent of the dilution.

Take as an example a substance with dissociation constants $k_a = k_b = 1.2 \times 10^{-7}$ (at 25°C.).

It will be found that in this case the degree of dissociation is 52 per cent. at all dilutions. This means that a substance which is simultaneously an acid 100 times weaker than acetic and a base 100 times weaker than ammonia acts nevertheless as a fairly good electrolyte.

It is obvious from the foregoing consideration that the reason why those acids such as glycollic do not obey the simple Ostwald dilution law, is because that in addition to H^+ we have also another positive ion HX^+ having a different ionic velocity, and the quantity of this HX^+ is not negligible except as a limiting case. Thus for orthoaminobenzoic acid, with $k_a = 1.04 \times 10^{-5}$ and $k_b = 1.34 \times 10^{-12}$, the ratio of concentration HX^+ to H^+ at various dilutions is as follows :—

In liters $v =$	64	128	256	512	1024
$\frac{HX^+}{H^+}$	1.63	0.81	0.40	0.20	0.10

"Knowing¹ the concentration of the various ions and their ionic velocities, the molecular conductivity of the solutions can be calculated. Close concordance between the theoretical and observed results has been found with the 3 aminobenzoic acids, cacodylic acid, and asparagine." The (affinity) dissociation constants of a great many other amphoteric bodies have been measured (cf. *Chem. Soc. Report*, 1906, p. 20).

"The proper application of the theory of electrolytic dissociation has here explained away a class of apparent exceptions to the theory, the apparent divergence being due to an improper assumption, regarding the nature of the ions present" (Walker, *loc. cit.*).

In addition to organic amphoteric electrolytes, similar inorganic bodies also exist. Thus, take the case of aluminium hydroxide, $Al(OH)_3$. This will act as a base and neutralise an acid as in its reaction with hydrochloric acid. It will also act as an acid and dissolve in potash, giving potassium aluminate with

¹ Walker, *Reports of the Chem. Soc.*, 1904.

the evolution of hydrogen. If one assumes for simplicity that no intermediate stages exist, the *acidic dissociation* of aluminium hydroxide would be represented by—



and the *basic dissociation* by—



In a sense, water itself is an amphoteric substance, since it gives rise to H^+ and OH' .

THE IONISATION CONSTANT OF WATER.

As already frequently pointed out, the ionisation constant of water, K_w , is the product of the concentration in pure water of the two ions H^+ and $(\text{OH})'$ in moles per liter. Though the numerical value of K_w is extremely small, *i.e.* of the order 10^{-14} , it has been found possible to measure it by several independent methods, the results of which are in satisfactory agreement. The table on p. 325 gives a résumé of the attempts made to measure K_w , the method, and date.

The methods may, therefore, be divided into :—

- (1) Direct conductivity of purest sample of H_2O .
- (2) Catalytic effects of H^+ and $(\text{OH})'$ in the saponification of methyl acetate ; muta-rotation of glucose.
- (3) From hydrolysis of salts, *e.g.* sodium acetate.
- (4) Electromotive force measurements.
- (5) There is also a method depending on the rate of change of conductivity of pure water with temperature which when compared with the heat of neutralisation of acids and bases affords strong grounds for supposing that the conductivity of pure water is due to H^+ and $(\text{OH})'$ in certain proportions. It deals, however, more particularly with the change of K_w with temperature.¹

The following is a slightly more detailed account of the above methods :—

- (1) *Conductivity Method*.—Kohlrausch and Heydweiller

¹ Cf. Heydweiller, *Ann. der Physik*, [4] **28**, 512, 1909.

[H'] = [OH'] in gram-moles per liter $\times 10^7$.	Temp.	Author.	Date.	Method.
[6.0]	25	Ostwald, <i>Zeitsch. physik. Chem.</i> , 11 , 521.	1893	Conductivity of pure water.
[9.4]	?	Ditto		Alkali and H ₂ cell.
1.1	25	Arrhenius, <i>ib.</i> , 11 , 823. Shields, <i>ib.</i> , 12 , 184.	1893 ,,	Hydrolysis of sod.-acetate, measured by ester saponification.
[0.1]	11	Wijs, <i>ib.</i> , 11 , 492.	1893	Saponification of methyl acetate by H ₂ O.
[6.0]	25	Bredig, <i>ib.</i> , 11 , 829. Cf. Arrhenius, <i>ib.</i> , 5 , 19, '90. Cf. Walker, <i>ib.</i> , 4 , 334, '89.	1893	Hydrolysis of aniline acetate from conductivity measurements.
1.2	25	Wijs, <i>ib.</i> , 12 , 514.	1893	Saponification of methyl acetate by H ₂ O.
0.8	18	Nernst, <i>ib.</i> , 14 , 155.	1894	Acid, alkali, H ₂ cell.
1.05	25	Kohlrausch & Heydweiller, <i>ib.</i> , 14 , 330.	1894	Conductivity of pure H ₂ O.
1.2	25	Löwenberz, <i>ib.</i> , 20 , 293.	1896	Acid alkali H ₂ cell.
0.91	25	A. A. Noyes & Kanolt, <i>Carnegie Inst. Pub.</i> , 63 , 297.	1907	Hydrolysis of ammonium-diketo tetrahydrothiazole by conductivity.
1.0	25	Hudson, <i>J. Amer. C. S.</i> , 29 , 1571 (1907); <i>ib.</i> , 1578 (1908). Circular No. 45, U.S. Dept. of Agriculture.	1909	Muta rotation of glucose by acids and alkalies.

determined the conductivity of water which had been freshly distilled *in vacuo* in platinum and sparingly soluble glass vessels, the specific conductivity observed at 18° C. being 0.04×10^{-6} reciprocal ohms.

Now this is due to the product of the number of ions (H' and (OH)') present into their mobility, *i.e.*—

$$0.04 \times 10^{-6} = n \times (U + V) = n(318 + 174)$$

$$\text{or } n = \frac{0.04 \times 10^{-6}}{492} = 0.8 \times 10^{-10} \text{ gram ions per c.c.}$$

Hence concentration of H' or OH' per liter is 0.8×10^{-7} , and therefore—

$$K_w = [H'][OH'] = 0.64 \times 10^{-14}$$

(2) *Method of Methyl Acetate Catalysis*.—The saponification of methyl acetate may be represented¹—



For every equivalent of OH' which thus disappears an equivalent of H' must be formed, because their product is constant. Thus we have acetic acid produced which in the earlier stages of the reaction may be regarded as completely dissociated. Now separate experiments on the saponification of the ester by acids and alkalies have shown that the effect of OH' was 1400 times greater than that of H' . The effect of the H' must be, of course, a purely catalytic one; that is, it probably by its catalytic power causes a water molecule to attack the ester, the H' remaining at the same concentration throughout. The OH' is actually used up in the ordinary way as shown by the equation given above.¹ If the process is as outlined, then, taking the case of ester in water, the decomposition starts with a certain velocity, which decreases owing to the disappearance of OH' . When the reaction is further advanced, however, the catalytic effect of the H' begins to more than compensate for the diminishing OH' , and the reaction constant begins to increase. It must, therefore, pass through a minimum. Wijs verified this directly by conductivity measurements (by measuring the rate of change of acetic acid formation per minute at different times).

Let us suppose the concentration of ester to be kept constant—this condition being practically fulfilled in the earlier stages of the experiment. Then the velocity of saponification is given by—

$$\frac{dx}{dt} = k_1[(OH)'] + k_2[H']$$

¹ It is not certain yet what the actual mechanism of the reaction is. An H_2O molecule catalysed by the OH' may be the actual reacting substance, the acetic acid formed being neutralised by the alkali.

where k_1 and k_2 are the velocity constants for saponification by OH' and H' respectively at constant ester concentration. At the minimum velocity point, the rate of change of the velocity, i.e. $\frac{d}{dt}\left(\frac{dx}{dt}\right)$ must be zero, that is—

$$\frac{d^2x}{dt^2} = k_1 \frac{d[\text{OH}']}{dt} + k_2 \frac{d[\text{H}']}{dt} = 0 \quad . \quad . \quad (1)$$

Now, from the ionisation equation for water, it follows that—

$$[\text{H}'][\text{OH}'] = K_w$$

and hence
$$\text{H}' \frac{d[\text{OH}']}{dt} + [\text{OH}'] \frac{d[\text{H}']}{dt} = 0 \quad . \quad . \quad (2)$$

must be fulfilled at any instant.

In order that (1) and (2) may simultaneously hold good, it is evident that—

$$\frac{[\text{H}']}{[\text{OH}']} = \frac{k_1}{k_2} \text{ which is known to be } = \frac{1400}{1}$$

This value for the concentration ratio is the criterion for the minimum velocity point. Now it is necessary to determine the acetic acid produced at the minimum velocity point (say, by conductivity measurements). The acid was found to be of the order 10^{-6} normal at this point, and assuming complete dissociation of the acid, this gives us the actual $[\text{H}']$, and since we know that the OH' is $\frac{1}{1400}$ of this, their product is easily calculated and hence K_w is obtained. The value obtained by Wijs in this manner is—

$$K_w = 1.96 \times 10^{-14}$$

K_w from the Catalytic Muta-Rotation of Glucose (Hudson, *Journ. Amer. Chem. Soc.*, **29**, 1571, 1907; *ibid.*, **31**, 1136, 1909).—Hudson measured the rate of change by means of the change of rotation in a polarimeter. The temperature was 24.7°C . The solution was made acid by HCl , thus furnishing a known amount of H' ion. The following are a few of his figures:—

Concentration of HCl.	Polarimeter reading at time (in minutes).								<i>k</i> .
	0'.	5'.	15'.	25'.	35'.	45'.	60'.	∞.	
0 (water alone)	32.8	30.8	28.4	25.8	24.2	22.8	21.5	17.7	0.0106
0.001									0.0098
0.005									0.0112
0.10	31.4	27.0	23.7	21.9	20.4	19.6	—	17.8	0.0354

The velocity of rotation increases with increase in H^+ ion. Osaka (*Zeitsch. physik. Chem.*, **35**, 702, 1900) found a similar relation in alkaline solution, but the catalytic¹ effect of OH^- is much greater than that of H^+ ion. Hudson finds the simple assumption to hold, viz. that simultaneous effect of both ions is simply additive, *i.e.*—

$$k = A + B[H^+] + C[OH^-]$$

It will be noted that in very weak acid solution (0.001N HCl) k is less than that in pure water. The same phenomenon occurs in methyl acetate, and is due to the same cause, *i.e.* depression of $[OH^-]$ owing to the presence in excess of the much less catalytically active H^+ ion. The difference in catalytic effect is shown by the value of the constants B and C. Hudson found—

$$B = 0.258, C = 9750$$

In pure water, let the velocity constant of muta-rotation be k_0 , then—

$$k_0 = A + (B + C)[H^+], \text{ for } [H^+] = [OH^-]$$

That is $[H^+] = \frac{k_0 - A}{B + C}$

From Hudson's and Osaka's results A, B, C and k_0 are known, and hence the $[H^+]$ can be obtained. The result is—

$$[H^+] = 1.0 \times 10^{-7} \text{ gram ions per litre}$$

$$\therefore K_w = 1.0 \times 10^{-14}$$

Hudson remarks that the accuracy of the method depends on the accuracy of determining the difference $k_0 - A$, which in the case of glucose is not large, being only about 10 per cent.

¹ The mechanism possibly involves the formation of a saccharate. Nothing is definitely known, however.

of the quantities themselves. Hudson considers the error in the result may be as much as 20 per cent. Experiments with fructose show that $k_o - A$ is much larger, and hence the result should be more accurate.

(3) *Method depending upon the Hydrolysis of Salts.*—It is necessary to determine the hydrolytic constant K_{hy} , say, of sodium acetate in water. Then K_w can be got from the relation $K_{hy} = \frac{K_w}{k_a}$, where k_a refers to acetic acid (see page 295). Or we may proceed as follows:—

A solution of sodium acetate $\left(\frac{N}{10}\right)$ was found by Shields to be hydrolysed to the extent of 0.008 per cent., or the salt gives rise to 0.000008 mole per liter of acetic acid (practically undissociated in presence of much acetanion) and 0.000008 mole of NaOH completely dissociated, *i.e.* 0.000008 mole OH' .

$$\text{Now } k_a \text{ for acetic acid} = \frac{[CH_3COO'] [H']}{[CH_3COOH]}$$

and from separate experiments k_a is found to be 1.78×10^{-5} . Now in the partially hydrolysed salt practically all the CH_3COO' present may be ascribed to the *salt*, which is practically completely dissociated (only an extremely small quantity of CH_3COO' is due to the acid). The concentration of $(CH_3COO)'$ may be put equal to 0.1 gram ion per liter.

$$\begin{aligned} \therefore [H'] &= \frac{k_a [CH_3COOH]}{[CH_3COO']} = \frac{1.78 \times 10^{-5} \times 8 \times 10^{-6}}{0.1} \\ &= 1.42 \times 10^{-9} \end{aligned}$$

$$\begin{aligned} \text{Hence } K_w &= [H'] [OH'] = 1.42 \times 10^{-9} \times 8 \times 10^{-6} \\ &= 1.136 \times 10^{-14} \end{aligned}$$

(4) *Electromotive Force Methods.*—These will be dealt with later (Part II. (Vol. II.), Chapter VII.).

(5) *Variation of K_w with Temperature.*—From a comparison of the variation of conductivity of the purest water with temperature (due to increased dissociation and increased mobility of the ions), with the heat of neutralization of strong

bases and acids, which is the heat of formation of water or its heat of dissociation with reversed sign, Heydweiller has recently obtained the following values for K_w at various temperatures:—

$t^\circ \text{C.}$	0°	10°	18°	25°	50°	100°	150°	200°
$K_w \times 10^{14}$	0.116	0.281	0.59	1.04	5.66	58.2	234	525

This method cannot be gone into here in detail, because it involves a thermodynamic relation between K and Q , the heat of neutralisation, namely—

$$\frac{d \log K}{dt} = \frac{-Q}{RT^2}$$

(an expression known as the van 't Hoff isochore). It should be noted how very great is the temperature coefficient. On the basis of the above equation, Arrhenius calculated what the temperature coefficient of K_w would be, and predicted its remarkable magnitude (see Arrhenius, *Textbook of Electrochemistry*).

ELECTROLYTIC EQUILIBRIUM IN SOLVENTS OTHER THAN WATER.

This can only be briefly touched upon—chiefly because of the absence of any comprehensive generalisations. Many apparently contradicting phenomena have been observed, and the existence of such is the main argument advanced by the opponents of the Electrolytic Dissociation Theory.

It will be remembered that according to the Nernst-Thomson Rule, electrolytic dissociation of the solute and polymerisation of the solvent itself are connected with the dielectric constant of the solvent, a solvent of large dielectric constant giving rise to large dissociation of the solute. This is not always the case.

In general one may see—especially with regard to organic solvents—that electrolytic dissociation is much less than in the case of water. The determination of the degree of dissociation

is, however, by no means an easy matter—the difficulty being to determine Λ_{∞} . Salts and “strong” acids or bases are not necessarily completely dissociated, even at great dilution, in many organic solvents, and of course may not be dissociated at all in many cases.

The value of α has, therefore, to be obtained by some other method, say, by lowering of freezing point or rise of boiling point, since the abnormal number of individuals present (if ionisation has taken place) is indicated by abnormal lowering of freezing point or rise of boiling point. These methods are not in general very accurate, and further, even in cases in which the accuracy is presumably fair, we meet occasionally with results which seem to prove that no dissociation has taken place, while at the same time the conductivity which the solutions possess is evidence that such must exist. Such facts, however, may be explained without giving up the principle of ionisation by considering the change in the polymerisation of the solvent which occurs simultaneously with changes in the molecular state of the solute. In fact, the most characteristic phenomenon in connection with non-aqueous solutions is the manifestation of solvent effects which only play a secondary rôle in aqueous solutions.

Sometimes, say, in the case of electrolytes in acetone, the molecular conductivity comes out much larger than the value at the same dilutions in water. Other evidence (cryoscopic, etc.) goes to show that the actual dissociation of the solute is considerably less than it is in water. This has been traced to the influence of the viscosity of the solvent. Thus the viscosity η of acetone is only about one-third that of water, and hence, to take a particular instance, the values of Λ_{∞} of AgNO_3 in acetone comes out to be a number over 350, while in water it is only a little over 115.

One important generalisation which is at least approximately true, in connection with Λ_{∞} , has been brought out as a result of the work of Dutoit, Friderich, Jones, Carrol, and Walden, namely, that Λ_{∞} of a solute is inversely proportional to the viscosity of the solvent, or—

$$\Lambda_{\infty} \times \eta = \text{constant independent of solvent.}$$

Walden verified this relation in the case of tetraethylammonium iodide when dissolved in a whole series of organic solvents, such as acetone, acetonitrile, ethyl chloride, methyl alcohol, nitromethane, acetic anhydride, benzaldehyde, furfuran, nitrobenzene, diethyl- and dimethyl-sulphate, formamide cyanacetic ester, etc. Further, Walden found this constant to be independent of temperature, which shows that the negative temperature coefficient of viscosity is numerically equal to the positive temperature coefficient of conductivity.

This generalisation can scarcely be regarded as very strictly accurate, for in many cases it is extremely difficult or impossible to determine Λ_{∞} , owing to the small degree of dissociation of solutes at ordinary dilution in organic solvents. That there is a connection at all between the conductivity of a solution and the fluidity of the solvent, *i.e.* the reciprocal of η , points to the supposition that the ions must be to a greater or less extent surrounded with an atmosphere of solvent molecules which they carry along with them, and hence their friction is the inner friction or viscosity of the solvent. We have already met with the phenomenon of hydration in the case of LiCl (notably) in water, as shown by the result of transport number determinations, and it appears that "solvation" in general, *i.e.* union of solvent and solute, frequently occurs.

From the above-mentioned results it is evident that solutes can exist in a partially ionised state in solvents other than water. Do these solvents themselves show any dissociation, even to a slight extent, such as occurs in the case of water? No definite evidence is forthcoming; if such exists the corresponding ionisation constants of the organic solvents must be still smaller than that of water. A further question is this. When reactions take place between substances, *i.e.* salts in organic solvents, does this presuppose ionisation?—in fact, do such reactions occur only between ions, or can undissociated molecules take part? Our experience with solutions in water is strongly in favour of the existence of ionisation as a necessary condition for chemical reaction, but in organic solvents this is more a matter of conjecture, though one is

inclined to think that something of the kind takes place. The possibility that molecules can react must, however, be kept clearly in view—see, for example, the paper by Miss Burke and Donnan, on the interaction of alkyl iodides and silver nitrates (*Zeitsch. physik. Chem.*, **69**, 148, 1909).

The Law of Mass Action (the Dilution Law).—The evidence as to whether this law holds or not in solvents other than water is conflicting. Thus Wakemann (*Zeitsch. physik. Chem.*, **11**, 49, 1893) found that for strong electrolytes in mixtures of ethyl alcohol and water the law did not apply, *i.e.* the behaviour is the same as in the case of water. Wilderman (*ibid.*, **14**, 247, 1894) found that in the case of trichloroacetic acid (a strong acid) in absolute alcohol the dilution law held good. Carrara has found that the behaviour of methyl alcohol as a solvent is very similar to that of water, *i.e.* strong electrolytes disobey the law, weak electrolytes are in agreement with it. Rudolphi's Law holds, however, for strong electrolytes. Cohen (*Zeitsch. physik. Chem.*, **25**, 5, 1898), finding from the work of previous investigators, and likewise his own results, that neither the Ostwald Dilution Law nor that of Rudolphi held good in the case of a number of inorganic salts dissolved in ethyl alcohol and aqueous alcohol mixtures, comes to the conclusion that the ratio $\frac{\Lambda_v}{\Lambda_\infty}$ is not a correct measure of the degree of dissociation.

On the other hand, Godlewski (*Journ. de Chim. Phys.*, **3**, 492, 1899) finds that for certain acids dissolved in ethyl alcohol and alcohol-water mixtures the dilution law holds good, the dissociation being calculated by the ratio $\frac{\Lambda_v}{\Lambda_\infty}$.

To show the influence of the gradual change in the nature of the solvent, the following data of Godlewski are given:—

(Godlewski investigated the behaviour of several acids other than salicylic and in general obtained similar results. The acids examined are weak (in aqueous solution).)

SALICYLIC ACID, 25° C.

Solvent % alcohol.	% Dissociation of $\frac{N}{64}$ solution.	Dissociation constant of acid (Ostwald's Dilution Law) $\times 10^5$.
0 { <i>i.e.</i> 100 % H ₂ O	22.1	100.0
10	21.9	95.5
20	20.6	83.0
30	17.3	57.2
40	13.1	31.6
50	10.1	17.8
60	8.11	11.0
70	5.31	4.59
80	3.33	1.75
90	1.94	0.579
100	0.291	0.013

It may be noted that salicylic is one of the few acids which are fairly largely dissociated in *water*, *i.e.* at $v = 1024$ liters $a = 62.8$ per cent., and yet it gives a dissociation constant.

Similar results were obtained with cyanacetic and bromoacetic acids. Again it has been shown that the maximal conductivities (*i.e.* the equivalent conductivities at infinite dilution) in the case of KI, NaCl, KCl, sodium salicylate, sodium cyanacetate, pass through a *minimum* value at 80 per cent. alcohol, the variation of Λ_∞ with alcohol content being observed over the range 0 to 100 per cent. alcohol. This suggests some kind of solvent complex formation which manifests itself in a viscosity-maximum of the solvent. That this maximum in viscosity, however, is not always the cause of the change in conductivity is shown by the work of Jones and his pupils in connection with certain salts dissolved in mixtures of water, methyl alcohol, ethyl alcohol, and acetone. Thus for LiNO_3 and $\text{Ca}(\text{NO}_3)_2$ a marked maximum in conductivity manifests itself in the case of the mixture acetone + ethyl alcohol (of certain composition), while the viscosity for varying compositions of mixed solvent is a straight line. This is ascribed by the authors to a change in the effective volume of the ions of the salt—the ions being solvated to different extents.

Kohlrausch's Law of the mobility of ions seems to break down in many cases in solvents other than water. Thus

Carrara found that in methyl alcohol, as in water, the ions of the halogens and sodium and potassium have mobilities which are concordant when calculated from their different salts, NaCl, NaBr, KCl, KBr; on the other hand, when the salts contain the cations, NH_4 , tetramethyl-ammonium, or sulfonium, the same anions appear to have different mobilities, *i.e.* the mobility does not appear to be independent of the salt from which it is produced.

For further study of non-aqueous solutions the following should be consulted:—

1. "Elektrochemie der nichtwässrigen Lösungen," by G. Carrara; translated by K. Arndt (*Ahrens Sammlung*, 12, 1907).

2. "The present Status of the Solvate Theory," by H. C. Jones (*Amer. Chem. Journ.*, 41, 19-57, 1909).

3. The work of P. Walden in the *Zeitsch. phys. Chem.*, from the year 1905 onwards.

4. The work of Hantsch on H_2SO_4 as a solvent (*Zeitsch. phys. Chem.*, 61, 297, 1907); also Bergius, *ib.* 72, 352, 1910.

WATER AS A SOLUTE.

The following is a short abstract¹ of a paper by P. Walden, *Trans. Far. Soc.*, 6, 71, 1910.

"We begin with the following three facts:—

"(1) The ionising power of a solvent stands directly in proportion to its dielectric capacity. This is the Nernst-Thomson rule. Walden's own experimental investigations on the molecular conductivity and on the degrees of electrolytic dissociation in non-aqueous solutions have given results which [in the main] are in accordance with this rule.

"(2) Water which forms polymerised molecules (Ramsay and Shields, etc.) [when alone], gives in all solvents—at small concentrations—only molecules of the form H_2O (Bruni and Amadori, *Trans. Far. Soc.*, V., 1910).

"(3) Water is also an electrolyte undergoing the electrolytic dissociation $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}'$.

"At the present time we possess a great number of ionising

¹ With some slight modifications, indicated thus [].

organic and inorganic solvents, which are characterised by an extremely high dissociating power towards binary salts, and in accordance with this fact also, by very high dielectric constants. Such solvents are HCN (dielectric constant, $K = 95$), formamide ($K > 84$), H_2SO_4 ($K > 84$). These three solvents, therefore, possess a greater ionising power than water, because their dielectric constant is higher than that of water ($K = 80$). [Now the question arises] Is *water* a good conductor in such solvents?"

Walden found that the conductivity due to H_2O when dissolved in HCN is extremely small. Some of his data may be quoted.

Temp. = 0° C. Specific conductivity of pure HCN is 0.657×10^{-5} reciprocal ohms. The values given are corrected for this quantity. v stands for the dilution of HCN in liters which contains 1 mole of water.

v .	Specific conductivity (corrected).	Equivalent conductivity of solution.
6.38	0.132×10^{-3}	0.00845
15.60	0.082×10^{-3}	0.0128
18.80	0.082×10^{-3}	0.015

"When we compare the conductivity of the electrolyte water with the conductivity of a binary salt (say KI) in HCN as solvent, we perceive the enormous difference between these two electrolytes:—

KI AS SOLUTE IN HYDROCYANIC ACID, $T = 0^\circ$ C.

v .	12.04.	27.07.	81.57.	
Λ_v	254	278	300	{ Kahlenberg and Schlundt.

v .	8.	16.	32.	
Λ_v	258	265	273	Centnerszwer.

Walden also found that H_2O dissolved in formamide and in formic acid is a very poor conductor. "On the other hand, we must accentuate the fact that formic acid with the lesser ionising power ($K = 58.5$) gives a higher conductivity [for dissolved water] than formamide with its greater ionising power (dielectric constant > 84). In nitrosodimethylamine, $\text{CH}_3 > \text{N}-\text{NO}$, as solvent ($K = 53.3$) water scarcely conducts, and indeed conducts less than in formic acid, although the dielectric constants are practically the same and the viscosity of formic acid is about double that of the nitroso body. The results, therefore, lead to the following anomalous conclusions:—

"(1) Water dissolved in the solvents HCN , HCONH_2 , HCOOH , and $\text{CH}_3 > \text{N}-\text{NO}$, shows in all these solutions very little conductivity.

"(2) The *smallest* numerical values of the conductivity were found in the solvents with the *highest* dielectric constant, and this further in spite of the great fluidity (for example in the solutions of HCN).

"(3) The highest values of the conductivity were observed in the solvent formic acid, which has a smaller fluidity and a smaller ionising power [*i.e.* slightly smaller K] than, for example, hydrocyanic acid.

"In the face of such results we must now ask the question: What is the cause of this anomalous behaviour of the water?

"Instead of a direct answer, we can only put forward an hypothesis. When all *physical* conditions were favourable to the existence of considerable electrolytic dissociation and great electrical conductivity of the solute, and nevertheless we have found small numerical values, then it seems to me [*i.e.* Walden] we must attempt a *chemical* interpretation of such anomalous results. Do they not stand in causal connection with the *chemical nature* of our solvents and water as the electrolyte? In short, is it not possible and probable that a body which is not *itself* an electrolytic conductor in the liquid state becomes, when dissolved, an electrolyte, if between this solute and the

solvent there exists a *chemical contrast*? When such a contrast exists, the solute and the solvent will give a (more or less stable) molecular combination of a *salt character*.

"These conceptions are in agreement with the proposition of Hittorf, stated by him half a century ago (1859): 'All electrolytes are salts.' If we accept these views as a working hypothesis, we must conclude that water as an amphoteric body [H^+ and OH^+ groups] will only become an electrolyte and a better conductor when it is dissolved in a liquid of a *distinctly acid or basic character*, that is, when it will form with this solvent a *kind of salt*."

This conclusion is amply borne out by experiment. We have already seen that formic acid as solvent dissociates water more than HCN or $HCONH_2$, although the dissociation is still small, in formic acid as solvent *i.e.* Λ_v varies from 0.15–0.17 for $v=2$ to $v=21$. Employing H_2SO_4 as solvent, Bergius found the following values for the equivalent conductivity of H_2O dissolved:—

v .	1.88.	2.53.	6.9	27.0 liters.
Λ_v	17.8	54.7	56.6	73.4

"It is evident that only the strong acid solvents (H_2SO_4 and $HCOOH$) give a considerable conductivity to the dissolved water; the stronger the acid character of the solvent (*e.g.* H_2SO_4) the higher is the conductivity of the water." Although HCN has a very high dielectric constant and a very small viscosity, it is quite unable to ionise H_2O molecules because the solvent itself is almost neutral (being an extremely weak acid). Obviously these conclusions must hold good for the reversed case. Thus, if water is the solvent, the best conducting solutions ought to be those of H_2SO_4 , the worst being those of HCN , because in the first case there is the marked chemical contrast which is absent in the second. As we have already seen, this is likewise borne out by experiment; HCN is one of the weakest acids when dissolved in water,

giving a very small dissociation constant. H_2SO_4 in water is so strongly dissociated that it gives no constant at all. It must be pointed out that these conclusions of Walden really represent a considerable modification of the simple dissociation theory; they do not, however, require that it should be discarded. The work here referred to brings out the importance of another factor in the mechanism of electrolytic dissociation, namely, *the chemical contrast of solute and solvent. In other words, the solvent is never really a neutral medium.* In the ordinary equations of the electrolytic theory, however, e.g. in the simple deduction of Ostwald's Dilution Law we consider the solute alone. It is evident from the above that we must also take into account the chemical nature of the solvent. How this general modification of the dissociation theory is to be carried out remains to be seen. At the present stage, however, it does not seem wise to discard the theory *in toto* as is done by Kahlenberg and others, solely on the ground of discrepancies—many of which (as in the case of Walker's explanation of amphoteric electrolytes) may be found on further examination to be actually explicable on the basis of the theory. There is hope, indeed, that the most striking anomaly with which the theory of electrolytic dissociation has to deal, namely, the behaviour of strong electrolytes, may after all be brought into line. As a further instance of the application of the theory of electrolytic dissociation to cases in which a definite rôle is assigned to the solvent, the reader is referred to the work of Bagster and Steele (*Trans. Faraday Soc.*, 8, 51, 1912) upon electrolysis in liquefied sulphur dioxide.

We have considered in some detail the theory of electrolytic dissociation in its application to homogeneous equilibria¹

¹ An important field of investigation has not been discussed owing to the relatively small advance which has been made up to the present time as regards a sound theoretical basis, namely, the so-called neutral salt action. The presence of, say, NaCl in a solution of HCl in certain cases increases "the activity of the H^+ ion," as regards its catalytic effect just as though it had actually *increased* the dissociation of the acid instead of decreasing it, as one would have expected from the standpoint of mass action. This effect has been examined recently by Arrhenius and his pupils (A. D. C. Rivett (*Zeitsch. physik. Chem.*, 1913), H. S. Taylor

in liquid solutions. Further applications will be made later in discussing heterogeneous equilibria (*e.g.* solubility relations, the "solubility product" and its bearing upon chemical analytical methods, etc.) and chemical kinetics. It will also be necessary to return to the theory from the standpoint of thermodynamics. It may be well at this juncture, however, to refer the reader to a critical survey of the theory by Noyes, in an address at the St. Louis Exhibition, 1904, and later an address by G. N. Lewis before the American Chemical Society (also published in the *Zeitsch. physik. Chem.*, **70**, 212, 1910), entitled "The use and abuse of the ionic theory."

(*Zeitsch. Elektrochem.*, **20**, 201, 1914), and others). A definite catalytic effect is now attributed to the undissociated molecule as well as to the ion.

CHAPTER VI

Chemical equilibrium in homogeneous systems (*continued*)—Solid solutions.

SOLID SOLUTIONS.

RELATIVELY little is known about the solid state or the conditions of equilibrium which exist therein. It will be evident, too, from what follows, that the methods of investigation really deal with conditions which belong rather to heterogeneous equilibria (as, of course, strictly do all determinations already mentioned, of vapour pressure, lowering of freezing-point, or rise of boiling-point); and these will be taken up later as examples of such equilibria. In the first place, we must distinguish between crystalline solid solutions or mixed crystals and amorphous solid solutions, such as the mixtures of silicates constituting glasses. These latter have no definite melting-point, but pass by a process of gradual softening into the mobile liquid state. They are therefore looked upon as liquids—supercooled liquids—of very high viscosity. The fact that they are supercooled, and therefore unstable, is shown by the gradual transformation into the crystalline or true solid form, this being the process involved in the devitrification of glass. Since the change from the visibly liquid to the amorphous state is a gradual one, there is no reason for putting any limit to the applicability of the laws of solution to the amorphous “solid” state. The only difference is that the progress towards equilibrium in such a case must be extremely slow owing to the enormous viscosity.

We are at present, however, dealing with the true crystalline solid state. The first question is—does the solute in such a case lower the vapour pressure of the solvent? In this connection von Hauer and Lehmann noticed that hydrated

salts—a particular case being lead sulphite—which tend to effloresce, thereby indicating a high vapour pressure, effloresced to a less extent when some other sulphite, such as CaSO_3 or SrSO_3 , was present. Such *homogeneous* mixtures can be made by freezing out a solution containing both. The same effect was noted in the case of the mixture of iron alum and aluminium alum. The decrease in efflorescence shows the lowering of vapour pressure due to the solute, and hence the solution shows a behaviour analogous to liquid solutions.

Other work to which reference might be made is that of Speranski (*Zeitsch. physik. Chem.*, **46**, 70, 1903; *ib.*, **51**, 45, 1905), who measured the vapour pressures of solid solutions of p-dichlorobenzene with p-dibromobenzene, and of p-chlorobromobenzene with p-dibromobenzene. He concluded that “the regular laws which hold for liquid solutions also hold for solid solutions.” Perman and Davies (*Trans. Chem. Soc.*, **91**, 1114, 1907) have investigated the vapour pressures of naphthalene and dilute solid solutions of naphthalene with β -naphthol; and more recently the system camphor-borneol has been investigated in a similar manner by E. Vanstone (*Trans. Chem. Soc.*, **97**, 429, 1910). Some of the results obtained by Vanstone may be quoted here by way of illustration. The vapour pressures of camphor and borneol were determined separately by two methods—one a static method by direct readings of the barometric column; and secondly a dynamic method by drawing air across the substance, and analysing the final composition of the gas. The following results were obtained:—

CAMPBOR VAPOUR PRESSURE IN MILLIMETRES OF MERCURY.

Temp. °C.	Vapour pressure (barometric method).	Temp. °C.	Vapour pressure (air current method).
78·6	7·09 mm.	78·1	6·83 mm.
96·8	16·15 „	95·1	15·88 „
111·0	33·00 „	110·9	33·00 „
131·0	75·00 „	131·1	75·20 „
157·0	181·5 „	156·0	185·4 „

The agreement between the two methods is satisfactory.

BORNEOL VAPOUR PRESSURE.

Temp.	Vapour pressure (barometric method).	Temp.	Vapour pressure (air current method).
77.9	2.16 mm.	78.0	2.30 mm.
96.8	6.55 „	95.2	6.67 „
110.0	15.00 „	110.5	15.70 „
131.9	40.92 „	130.2	40.4 „
156.0	115.16 „	150.2	96.6 „
—	—	158.4	127.2 „

Solid solutions were then made simply by fusing the two substances in the required proportions—both solids are completely miscible. The following data refer to 110° C. :—

Mols borneol per 100 mols mixture.	Vapour pressure of solid solution determined by air-current method. (The barometer method results agree fairly well with these.)		
10	30.52	30.62	30.12
20	27.81		27.90
30	27.10		27.26
40	25.21		24.86
50	24.00		23.96
60	20.87		20.88
70	19.93		19.94
80	18.24		18.17
90	17.90		17.81
100	15.00		15.10
	(duplicate measurements)		

If we consider camphor as the solvent—it having the higher vapour pressure—it will be seen that the addition of the borneol causes a lowering of the vapour pressure somewhat in the same way as dissolved sugar lowers the vapour pressure of water. The case is, however, much more analogous to a mixture say of alcohol and water, for both constituents have measurable vapour pressures whose order of magnitude is much the same. In the ordinary simple cryoscopic expressions for determining the molecular weights of solutes, one of the main assumptions is that the solute shall be non-volatile compared to the solvent. When the solute is

volatile an expression for its effect on the vapour pressure of the solvent, as well as upon the freezing-point and boiling-point, can be obtained on thermodynamical grounds. This is evidently analogous to the case we are dealing with in the camphor-borneol system. Such systems as these, however, are much more conveniently considered under the section dealing with phase equilibria especially from the standpoint of the Phase Rule, to which important generalisation we shall come later.

A general conclusion which has been reached in connection with solid solutions is that the molecules of the solute are *not* polymerised more than in the liquid solution state, though one might have expected otherwise. Thus let us take the case of the mixed crystals of thallium nitrate and potassium nitrate investigated by Fock, *Ber.*, **28**, 408, 2734.

The potassium nitrate was present in the *aqueous* solution in large amount and at constant concentration. To this was added thalious nitrate in increasing quantities, the homogeneous solid mixed crystals of both salts which separated from the solution being analysed. The large amount of KNO_3 in the liquid solution threw back the dissociation of the TlNO_3 , so that we are dealing mainly with undissociated molecules. Some of the results obtained at 25° are as follows:—

Concentration of $\text{TlNO}_3(c_1)$ in the liquid solution.	Concentration of KNO_3 in the liquid.	TlNO_3 molecular per cent. ¹ in the solid $= (x_1)$.	$\frac{c_1}{x_1}$.
0·3238	3·2658	2·77	0·117
0·1869	3·2944	1·78	0·105
0·0663	3·2981	0·57	0·116
0·0231	3·2851	0·20	0·116
0·0089	3·2515	0·08	0·111

From the above it will be seen that the concentration of the TlNO_3 in the mixed crystal is proportional to its concentration in aqueous solution. Now, from considerations in connection with

¹ Molecular per cent = number of gram-molecules of TlNO_3 in 100 gram-molecules of the mixture.

the Distribution Law, to which frequent reference will be made later in connection with heterogeneous equilibria, it can be shown that when the ratio of the concentrations of a given substance distributed between two phases is constant, *i.e.* independent of the absolute amount dissolved in the phases, then the substance which is undergoing distribution must have the same molecular weight in the two phases. Since we know that the molecules of TiNO_3 are simple in the aqueous solution they must also be simple in the mixed crystal.

We can also take a few examples from the crystalline mixtures exhibited by some non-electrolytes. Thus, take the case of iodine and benzene.¹

On freezing out a part of a solution of benzene which contains iodine, the pure benzene does not separate out alone, but always admixed with some iodine. The connection between the concentration of iodine in the liquid benzene and that in the solid is as follows :—

Liquid solution Concentration of iodine	Solid solution Concentration of iodine	Ratio [iodine] in solid [iodine] in liquid
3.39 per cent.	1.279 per cent.	0.377
2.587 "	0.925 "	0.358
0.945 "	0.317 "	0.336
		Mean 0.357

Since the ratio is approximately constant, for reasons just given it follows that the molecular weight of iodine is the same in liquid as in solid benzene. Since it is known in liquid benzene to have the molecular weight corresponding to I_2 , it must also exist in the solid mixed crystal as I_2 . Exactly similar relations are found in the case of benzene and thiophene, *i.e.* the latter is $\text{C}_4\text{H}_4\text{S}$ both in liquid benzene and in solid benzene.

In certain cases we may even find that in the mixed crystal one of the components has a smaller molecular weight than in the ordinary case. Thus take the case of hydrogen

¹ Van 't Hoff's Lectures, II. 75.

gas and palladium. These are supposed to form a compound, a hydride which mixes homogeneously with the metal. [Details of this particular instance will be taken up in discussing heterogeneous equilibria, as there are certain peculiarities which call for remark.]

The following data show the connection between the concentration of the hydrogen in the gaseous form and that in the metal in contact with the gas :—

(P) pressure of H ₂ gas (a measure of its concentration in the gaseous phase).	Volume of Pd in c.c. (<i>v</i>) which contains 2 mg. of hydrogen.	<i>Pv</i> .	$v\sqrt{P}$.
26·2	3·084	80·8	15·8
82·8	1·827	151·3	16·6
165·4	1·299	214·8	16·6
393·7	0·771	303·5	15·3

It will be seen that the concentration of hydrogen in the gas phase (measured by *P*) is not proportional to the concentration of gas in solid phase (measured by $\frac{1}{v}$), but that the square root of the concentration of the gas in the gas phase is proportional to the concentration of the gas in the solid phase. From consideration of the Distribution Law (a generalisation to be discussed under heterogeneous equilibria), the above behaviour can be explained by assuming that the hydrogen in the palladium exists as atomic hydrogen, H, not H₂.

The above instances quoted give a general idea of our knowledge of the chemistry of the solid state. It is evidently scanty. Reactions between solutes in the ordinary sense of the term, involving the final arrival at an equilibrium point, have not yet been investigated. The slowness with which reactions can proceed in most cases renders investigation impracticable. It must be clearly borne in mind that in the above cases of solid solution or mixed crystals, we are speaking of homogeneous mixed crystals. Of course, heterogeneous masses of crystals are common, but these are not "mixed" in the true sense. It can evidently happen that a

homogeneous state of mixed crystals can give rise to a heterogeneous mixture on altering some condition, such as temperature or concentration. We have frequent examples of this in metallic alloys. Thus, if we prepare some HgCd alloys (by heating the metals together), and allow the alloy to reach the ordinary temperature, it will in general solidify (provided enough Cd is present). If we do not exceed about 10 per cent. Cd, the resulting alloy is a homogeneous solid. If we exceed this amount of Cd, the solid generally disintegrates into a heterogeneous mixture with crystals of different type lying side by side. Or, again, if we start with pure molten iron and add a small quantity of carbon, we find the melting-point of the iron lowered. We also find on analysis that the solid at a given temperature in equilibrium with the molten solution contains some carbon, though at a smaller concentration than in the liquid state. This lowering of melting-point of the metal continues on further addition of the carbon up to the solubility limit of C in Fe. The solid which has separated out at various temperatures corresponding to a given carbon content is homogeneous—a homogeneous solid solution—but if this be allowed to cool down it becomes heterogeneous, giving rise to a solid having a different structure and different properties. This final state is not a solid solution.

A striking experimental test which can be applied to solid solutions is the following. Some of the powdered solid is placed inside a Geissler tube, which is evacuated and current passed through the tube, the cathode discharge being in active operation. Under these conditions the solid solution will fluoresce. No explanation has been offered of this remarkable phenomenon, though the phenomenon itself has been employed as a test of the degree of purity of certain rare earth preparations at the various stages of the separation—since usually a number of the rare earths are found together, presumably in a state of solid solution mainly.

For further information upon solid solutions the reader is referred to the monograph "Solid Solutions," by G. Bruni (*Ahrens Sammlung*, 6, 1901), also Desch's *Metallography* (Sir William Ramsay's Text-books of Physical Chemistry).

CHAPTER VII

Chemical equilibrium in heterogeneous systems from the kinetic standpoint, effects due to capillarity, radiation, etc., being absent—Nernst's Distribution Law—Gas-liquid systems—Liquid-liquid systems—Solid-liquid systems—Gas-solid systems—Solid-solid systems—Solubility and the "solubility product."

GENERAL CONSIDERATION OF HETEROGENEOUS EQUILIBRIA.

A HETEROGENEOUS system is one which consists of more than one physical state or *phase*, and the equilibrium of the phases and of the components amongst the different phases is termed heterogeneous equilibrium. Thus liquid water in contact with water vapour in an enclosed space at a given temperature is an instance of heterogeneous equilibrium. In this case if the temperature be kept constant, the pressure of the system, *i.e.* the vapour pressure, remains constant, as also does the amount of each phase for infinite time. Typical heterogeneous equilibria occur in the following cases :—

Gas in contact with liquid

Gas	„	„	solid
Liquid	„	„	liquid
Liquid	„	„	solid
Solid	„	„	solid

No heterogeneous equilibrium can exist between gas and gas, since all gases are completely miscible.

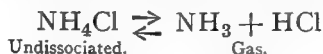
Heterogeneous equilibria are governed by two principles or generalisations : first that known as the DISTRIBUTION LAW, and secondly that known as the PHASE RULE. The latter is independent of any molecular theory being deduced from the principles of thermodynamics in which energy changes (as

opposed to molecular changes) accompanying any process are considered. The Phase Rule may be regarded as a comprehensive generalisation, which is rather qualitative than quantitative—in the sense that the law of mass action is quantitative.¹ In a sense it may be said to include the Distribution Law, though not explicitly. Let us consider these two principles briefly.

We are already familiar with the concept of a statistical equilibrium between molecules in a *homogeneous* system. Now in the case of liquid water in contact with saturated water vapour we may likewise consider that the equilibrium is statistical, being reached when the number of molecules passing from the liquid to the vapour in a given time is equal to the number passing in the opposite direction. The molecules of water may be said to distribute themselves between the two phases, the equilibrium being governed by a principle analogous to that of the Distribution Law. In the analogous case of a gas distributing itself between a solvent (water, say) and the space above the solvent, a statistical equilibrium with respect to the molecules of the gas is also set up. If the quantity of gas in the gas phase be doubled, then (in the simplest case) the quantity dissolved must also be doubled in order that the number of gas molecules passing from the gas phase to the solution per second shall be equal to the number passing in the opposite direction. Now doubling the quantity of gas in the gas phase at constant volume means doubling the gas pressure. This has caused the concentration of gas in the water to be doubled. In other words, the concentration of dissolved gas is proportional to the gas pressure. This is HENRY'S LAW (1803), which is thus seen to be a particular case of the Distribution Law. Now consider a somewhat different case—one in which a chemical reaction in the ordinary sense may take place in one of the phases (say the gaseous phase), and simultaneously a molecular distribution takes effect between the two phases. An example of this

¹ It would be better, perhaps, to say that the law of mass action involves a term, the "constant," characterised by a certain *numerical* value. The Phase Rule contains no analogous term.

type of heterogeneous equilibrium is afforded by the partial dissociation of ammonium chloride vapour in contact with the solid. The reaction in the vapour phase is—



and the law of mass action applied to the homogeneous gaseous phase requires that—

$$\frac{C_{\text{NH}_3} \times C_{\text{HCl}}}{C_{\text{NH}_4\text{Cl}}} = \text{constant (at a given temperature).}$$

The equilibrium expression assumes the existence of some undissociated NH_4Cl molecules in the gaseous phase, and the effect of the presence of the solid NH_4Cl is to cause the gas space to be saturated with respect to undissociated NH_4Cl molecules, and thus to cause the concentration of the undissociated gas molecules to remain constant (at constant temperature), so that the mass action expression becomes—

$$C_{\text{NH}_3} \times C_{\text{HCl}} = \text{constant.}$$

Such a reaction is always spoken of as a heterogeneous one, and the name is convenient. More strictly, however, the “chemical” reaction itself is a homogeneous one, modified by a distribution law effect in the case of one of the reacting substances of such a nature that the concentration of this substance is constant at constant temperature.

The concept of statistical molecular equilibrium does not cover, however, all the phenomena connected with heterogeneous equilibrium, coexistence of phases and continuity of state. Let us consider the case of liquid water in equilibrium with water vapour. We know that there is a wide range of temperature throughout which these two phases can co-exist, the vapour pressure altering continuously with the temperature. There is, however, a temperature limit (the critical temperature) beyond which such a type of equilibrium cannot exist. Thus we may raise the temperature of the liquid water-vapour system from 0°C. to 365°C. , and find a continuous series of equilibrium states, the equilibrium pressure rising finally to a very high value (200 atmospheres). Above the

critical temperature, however, heterogeneous equilibrium is impossible, and the homogeneous equilibrium which sets in is that of the spatial distribution of the molecules taken account of by the gas laws and equations of state. Again, if we consider the same system at low temperatures we find that at 0°C . (under atmospheric pressure) water in the *solid* form begins to separate out, and we thus obtain three phases: solid, liquid, and gaseous. At one single temperature, namely, 0.008° above zero, and under the pressure of the saturated vapour, we find these three phases co-existing in equilibrium. On slightly lowering the temperature, the liquid phase disappears, *i.e.* becomes solid, the system now consisting of solid and vapour between which over a wide temperature range (as far as we can measure it in fact) on the lower side of 0°C . we again find a continuous series of statistical equilibria set up. The statistical principle will not account for the *complete* transformation (disappearance) of a phase except as a possibility. Neither will it account for the fact that liquid, solid and gaseous H_2O , can only exist in equilibrium at a single temperature and pressure. This remarkable fact can, however, be anticipated on the basis of the principle known as the Phase Rule, which, as already mentioned, is based upon thermodynamical considerations. The Phase Rule predicts also that liquid water and vapour can co-exist in equilibrium over a temperature range, and similarly for ice and vapour and ice and liquid. It will not predict, however, that a critical point would be reached.

In addition to the equilibrium between a liquid and its saturated vapour, heterogeneous equilibrium is also set up between a solid and its saturated solution, or in the distribution of a substance such as picric acid between two immiscible solvents such as benzene and water in contact. This latter case is a typical instance of an equilibrium governed by the Distribution Law. In *any* case of heterogeneous equilibrium, the Phase Rule and Distribution Law are simultaneously operative; it is only for the sake of clearness that we consider them apart.

The first complete statement of the Distribution Law was

made by Nernst (*Zeitsch. physik. Chem.*, 8, 110, 1891). The following description is taken largely from the introduction to Nernst's paper.¹

THE DISTRIBUTION LAW.

If a substance possesses the same molecular weight in the gaseous and in the dissolved state, its partial pressure in the vapour, which is in equilibrium with the solution, is proportional to its concentration in the latter (*i.e.* the solution). Nernst calls this the law of van 't Hoff.

If a dissolved substance distributes itself between two different liquids which are only slightly miscible (*e.g.* iodine shaken up with water and carbon disulphide), the above law at once leads to a second, namely, that in the equilibrium state at a given temperature the *ratio* of the concentration of the dissolved substance in each solvent is independent of its absolute mass, or, in other words, the dissolved substance possesses a constant distribution coefficient when it possesses the same molecular weight in both solvents.

If several gases are present simultaneously in the same solvent, or several dissolved substances distribute themselves simultaneously between two given immiscible solvents, there is no effect upon the concentration ratio of any *one* of them (due to the presence of the others) presupposing the absence of any chemical interaction between molecules of different kind. That each single gas in a mixture of gases is absorbed in proportion to its own partial pressure was pointed out by Dalton; that mixtures of dissolved substances which do not react with one another, distribute themselves as though each were alone present in the system, has been shown by Berthelot (*Ann. Chim. et de Phys.*, [4] 26, 417, 1872) to be a completely analogous phenomenon to the Dalton Absorption Law. One can unite both the foregoing expressions into one, namely,

¹ As regards the *principle* of distribution, reference should be made to a paper by P. Aulich (*Zeitsch. physik. Chem.*, 8, 105, 1891), who stated the principle independently of Nernst some years previously (1887), though it is to the latter that we owe the real introduction of the idea into chemistry.

at a given temperature for each molecular species there exists a constant distribution ratio between two solvents or between one solvent and the vapour space in contact with it, no matter whether other molecular species are present or not.

The important extension which Nernst gave to the above principle is the following: The above law holds good (when correctly applied) even when a chemical reaction does take place between the different molecular species. For example, if we consider a substance which has undergone partial electrolytic dissociation in one of the solvents, existing thus as undissociated molecules and ions, then each species may still possess a constant distribution ratio (characteristic of itself). The principle is best understood by an example. Consider the distribution of succinic acid between water and ether. The acid is not dissociated at all in ether; the molecular weight is normal. In water it undergoes slight electrolytic dissociation. Nernst's idea is that a constant ratio is found for the concentration of the undissociated part of the acid in the water and the (total) acid in the ether, and this ratio is independent of the total mass of succinic acid in the heterogeneous system as a whole. The ions are not soluble in ether, and therefore for each of them the distribution ratio, if one can use the term, is also constant, being either 0 or ∞ .

A slightly more complex state of affairs is met with in the case of benzoic acid in certain solvents, *e.g.* benzene, in which a partial polymerisation of the acid occurs according to the equation



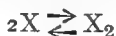
In water the same acid is not polymerised, but suffers a very slight electrolytic dissociation. If water and benzene are brought into contact, and benzoic acid allowed to distribute itself between the two, Nernst's principle states that for the simple non-dissociated unpolymerised molecules of acid present in each phase a certain distribution ratio holds good independent of the total mass of benzoic acid in the system as a whole. Neither the polymerised molecules nor the ions can be said to possess a distribution coefficient, it being either 0 or ∞ .

GAS-LIQUID SYSTEMS.

The modification of Henry's Law when the molecular state of the gas in the gas phase differs from that in the solution.

In obtaining the simple expression of proportionality between gas pressure and concentration of dissolved gas, it was assumed that the gas on dissolving underwent no chemical change (polymerisation or dissociation). Henry's Law is to be modified when such effects are present.

Let us suppose the dissolved gas is partly polymerised. In the solution, if we denote simple gas molecules by X and the polymerised molecules by X_2 , the reaction equilibrium we are considering in solution is



Applying the law of mass action we obtain at a given temperature

$$C_{X_2} = KC_X^2 \text{ or } C_X = \sqrt{\frac{C_{X_2}}{K}}$$

Now Nernst's extension of the van 't Hoff Law of Distribution states that direct proportionality exists between the concentration of like molecules in the two phases, or what is the same thing, there is direct proportionality between the gas pressure P (which is due entirely to simple X molecules) and the concentration C_X of the simple dissolved molecules. If we denote this proportionality factor by K' we can write the above statement in the form

$$P = K'C_X$$

Now substituting the value $\sqrt{\frac{C_{X_2}}{K}}$ for C_X in this expression, we obtain—

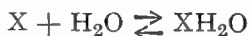
$$P = K'\sqrt{\frac{C_{X_2}}{K}}$$

and since $\frac{K'}{\sqrt{K}}$ is a constant, say K_2 , we obtain finally—

$$P = K_2\sqrt{C_{X_2}}$$

Now if practically all the dissolved gas molecules exist in the polymerised form X_2 the term C_{X_2} will very nearly represent the *total concentration of the dissolved gas*, so that in this particular case the concentration of the dissolved gas will be proportional to the *square* of the pressure of the undissolved gas. If the degree of polymerisation had been higher than 2, say n , so that the dissolved molecules of gas were represented by X_n , and if, further, practically all the gas dissolved were in this condition, then the concentration of the dissolved gas would be proportional to the n th power of the gas pressure. In the case of dissociation of X into smaller individuals the value of n would be less than unity, but the same distribution principle will hold good.

It is important to observe that union of the *solvent* with simple gas molecules X will not in any way alter the applicability of the simple Henry-van't Hoff Law. Thus suppose the solvent is water, and further suppose that some of the dissolved gas molecules are hydrated, the reaction, which is in equilibrium in solution, is



The law of mass action applied to this yields the relation

$$\frac{C_X \times C_{H_2O}}{C_{XH_2O}} = K$$

But if the solution is dilute the concentration of the solvent C_{H_2O} is constant, and we can therefore write—

$$\frac{C_X}{C_{XH_2O}} = K_1$$

Now the distribution equilibrium of the simple X molecules gives us the relation—

$$P = K'C_X$$

and combining this with the above we obtain

$$P = K'K_1C_{XH_2O}$$

where P is the gas pressure. Writing $K'K_1$ as K_2 we get—

$$P = K_2C_{XH_2O}$$

That is, the concentration of the hydrated molecules is proportional to the gas pressure, just as is the concentration of the unhydrated gas molecules. To state the Henry-van 't Hoff Law correctly we must therefore say:—

Direct proportionality exists between the gas pressure of a partly dissolved gas and the concentration of the dissolved gas when the latter exists either in the form of simple gas molecules or as hydrated gas molecules, the solution being a dilute one.

In the general case it will be evident that distribution experiments will give us useful information respecting the molecular state of dissolved substances.

LIQUID-LIQUID SYSTEMS.

Consider a substance distributed between two immiscible solvents. If chemical action is absent (polymerisation, dissociation), the distribution law takes the simple form—

$$\frac{C_I}{C_{II}} = \text{constant}$$

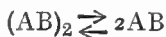
where C_I is the concentration of the solute in solvent I.
and C_{II} " " " " solvent II.

These concentration terms refer to the total solute present in a given volume of each phase. This was verified by Berthelot and Jungfleisch for the case of the distribution of bromine and iodine between water and carbon disulphide. The ratio remained constant even when the absolute values of the concentration terms varied from 1 to 10. Both elements possess normal molecular weights (Br_2 , I_2) in each solvent. When any chemical effect enters, such as polymerisation or dissociation, the distribution law expression—

$$\frac{C_I}{C_{II}} = \text{constant}$$

only holds for certain parts of the dissolved substance present in each phase, *e.g.* for the normal benzoic acid molecules in the case mentioned previously of the distribution of this acid. By

applying the law of mass action, however, to the equilibria conditions which are set up in one of the phases when distribution equilibrium has already been attained, it is possible to transform the distribution law expression into a shape which is, in certain cases more amenable to experimental verification. Let us take a case in which polymerisation of solute may occur to form double molecules in both solvents in contact, though to quite different amounts. In the first solvent suppose the double molecules are present to a small extent, their concentration being x and $(c_1 - x)$, the concentration of the normal molecules in the same solvent. Then the reaction—



when one applies the law of mass action to the case of the first solvent, yields the relation—

$$\frac{(c_1 - x)^2}{x} = K_1$$

where K_1 is the equilibrium constant of the reaction in the first solvent. Similarly, if we denote the simple molecules in the second solvent by y , and double molecules by $c_2 - y$, we obtain—

$$\frac{(c_2 - y)}{y^2} = K_2$$

According to the distribution law for the simple molecules one obtains—

$$\frac{c_1 - x}{y} = \text{constant} = k_1$$

and for the double molecules—

$$\frac{x}{c_2 - y} = \text{constant} = k_2$$

Hence
$$\frac{(c_1 - x)\sqrt{K_2}}{\sqrt{c_2 - y}} = k_1 \quad \text{or} \quad \frac{(c_1 - x)^2}{c_2 - y} = k_0$$

If now we are dealing with the case in which benzene is in contact with water, and an organic acid such as benzoic is distributed between the two, we know that on the benzene side

the concentration of simple molecules (y) can be neglected compared to that of the double molecules, and similarly on the water side the double molecules x can be neglected compared to the single molecules; and further, if we neglect the electrolytic dissociation, which is very small for the majority of organic acids, we find that the distribution law becomes—

$$\frac{c_1^2}{c_2} = k_0$$

where c_1 = the concentration of the undissociated normal benzoic acid molecules in the water (*i.e.* practically the entire solute present in the water);

c_2 = the concentration of the “double-moleculated” acid in the benzene, *i.e.* practically all the acid present.

The experimental verification of such conclusions as the above was undertaken by Nernst, notably in the case of acetic acid and phenol, which, according to freezing-point molecular weight determinations, are each normal in water, but very largely polymerised to double molecules in benzene (when the concentration is sufficiently large).

The Distribution of Acetic Acid between Benzene and Water.

—Nernst made use of the Beckmann freezing-point apparatus. 5.075 grams water were placed in the tube, and 31.5 grams benzene above it. The freezing-point of the mixture, *i.e.* the freezing-point of the benzene, was determined. Owing to the exceedingly small solubility of the water in benzene, the freezing-point was practically that of pure benzene, namely, 5.9° C. On adding successive quantities of acetic acid, which distributed itself between both solvents, the corresponding lowering of the freezing-point of the benzene layer was determined. This lowering corresponded to the quantity of acetic acid dissolved in the benzene; in order to determine this concentration term separate experiments were carried out with known quantities of acetic acid dissolved in moist benzene, and the corresponding freezing-points noted. The results are given in the following table, in which t represents the observed lowering of freezing-point; c_2 the number of grams of acetic

acid in benzene corresponding to t , and obtained by means of the separate experiments; c_1 the number of grams of acetic acid which were present in the 5.075 grams water (obtained by subtracting c_2 from the total amount used).

t .	c_2 .	c_1 .	$\frac{c_1}{c_2}$.	$\frac{c_1^2}{c_2}$.
0.075°	0.043	0.245	5.7	1.40
0.120°	0.071	0.314	4.4	1.39
0.158°	0.094	0.375	4.0	1.49
0.240°	0.149	0.500	3.4	1.67

It will be noted that $\frac{c_1}{c_2}$ is much less constant than $\frac{c_1^2}{c_2}$; since the latter increases with increasing concentration, we can infer that while acetic acid in benzene exists mainly in the form of double molecules at small concentrations, the number of single molecules cannot be neglected. Analogous results were obtained for the distribution of phenol between water and benzene, as well as the distribution of benzoic and salicylic acids between the same solvents. For details Nernst's paper should be consulted. A further account of distribution experiments and data will be found in an article by Herz in *Ahrens Sammlung*, vol. 15, 1910.

Determination of Hydrolysis (of Salts) by Distribution Measurements.—The principle of the method will be made clear by considering a specific case, namely, the hydrolysis of aniline hydrochloride. Suppose this salt dissolved in a certain volume v of water, and further suppose the degree of hydrolysis is x , then the concentration of the free aniline is $\frac{x}{v}$ gram molecules per liter. If now a layer of benzene of known volume be poured upon the water, the aniline will distribute itself between the two layers. The quantity of aniline present in the benzene can be estimated by analysis. Separate experiments with aniline itself distributed between water and benzene are carried out and the distribution ratio

determined. Knowing this ratio and the quantity of aniline actually present in the benzene layer above the aqueous solution of aniline hydrochloride, it is easy to determine the concentration of the aniline in the aqueous layer, and hence obtain x , the degree of hydrolysis. It is assumed that the quantity of aniline removed into the benzene layer is negligible compared to the quantity represented by x .

The Process of Extraction.—According to the distribution law, for a substance the molecular weight of which is identical in two immiscible solvents, the relationship holds good—

$$\frac{c_I}{c_{II}} = \text{a constant dependent only upon temperature.}$$

Let us suppose the concentration to go on increasing by successive addition of solute until the solubility s of the solute is reached in one phase, say in I. Then the distribution law says—

$$\frac{s_I}{c_{II}} = \text{constant}$$

But at a given temperature s is a constant, and therefore c_{II} must be a constant independent of the further quantity of solute added to the system; no further solution can take place in solvent I., and the distribution law makes c_{II} also constant, and hence c_I at this point must likewise be the limiting concentration, or the solubility of the solute in solvent II. Hence the distribution law may be put in form: the distribution of the solute at any concentration up to saturation takes place in the ratio of the solubilities of the solute in the phases.

Now, if we have an aqueous solution of an organic substance, and wish to extract the solute with a limited quantity of benzene (say), the question is, What is the most advantageous way to use the benzene? Should it be added all at once, or in successive small quantities? The best results as far as extraction is concerned are obtained by the second method. This will be seen from the following considerations. Suppose that the substance is twice as soluble in benzene as it is in water. The distribution law constant is therefore 2. If the

amount of the substance in 1 liter of water is A , and we add the whole of the benzene, say 1 liter, we shall have $\frac{A}{3}$ remaining in the water, and $\frac{2}{3}A$ in the benzene—this latter being the quantity extracted. Now suppose we employ the benzene in two equal stages. That is, to 1 liter of aqueous solution we add $\frac{1}{2}$ liter of benzene. Let x be the amount extracted. Then $A - x$ remains in the water, and—

$$\frac{\frac{x}{\frac{1}{2} \text{ (liter)}}}{A - x} \text{ must still be equal to } 2$$

that is

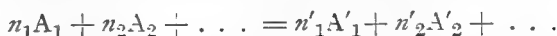
$$x = \frac{A}{2}$$

By using $\frac{1}{2}$ liter benzene we have extracted half the solute leaving half behind. On adding a fresh $\frac{1}{2}$ liter of benzene to the aqueous layer, we extract half of what remains of the solute; that is to say, $\frac{1}{4}A$, so that both operations have resulted together in the extraction of $\frac{3}{4}A$. In the previous case, with the same quantity of benzene, $\frac{2}{3}A$ was extracted. Hence the second process is the more advantageous. Theoretically an infinite number of extractions with infinitely small quantities of benzene would be the most advantageous conditions; but in practice considerations of time naturally come in.

Further Applications of the Distribution Law.—Nernst concludes his paper with certain considerations, to some of which reference will now be made. If one alters the extent of (electrolytic) dissociation of a volatile electrolyte in a liquid phase, then its vapour pressure (the partial pressure due to the solute) will be altered, as would also be its concentration in a second solvent if such be in contact. Thus the partial pressure of hydrochloric acid over its aqueous solution will *increase*, for example, when one adds to the solution a second electrolyte with a common ion (*e.g.* NaCl), and will *decrease* when the latter does not possess a common ion, since the vapour (HCl) consists of undissociated molecules in equilibrium with the undissociated molecules present in the solution. Again, salicylic acid in dilute aqueous solution

would pass over in large quantity into a benzene layer in contact when a strong acid or a salt of salicylic acid is dissolved in the aqueous layer. The addition of the latter causes some of the salicylic ions ($\text{C}_6\text{H}_4\text{OHCOO}'$) to unite with the H' ions to form a number of undissociated molecules of acid, and since there must be a constant distribution ratio for these undissociated molecules between the two solvents, it follows that their concentration in the benzene layer must increase also; that is, some further salicylic acid passes from the aqueous into the benzene layer.

Consider now a general case of a solution containing a number of substances which are volatile, and let a chemical reaction between the solutes take place as follows—



Suppose equilibrium is established when the partial pressures of the different species are $p_1 p_2 \dots p'_1 p'_2 \dots$, and their concentration terms are $c_1 c_2 \dots c'_1 c'_2 \dots$. Then applying the law of mass action to the two phases—solution and vapour—we obtain—

$$\frac{p_1^{n_1} p_2^{n_2} \dots}{p_1^{n'_1} p_2^{n'_2} \dots} = K \quad (\text{for the vapour phase})$$

$$\frac{c_1^{n_1} c_2^{n_2} \dots}{c_1^{n'_1} c_2^{n'_2} \dots} = K' \quad (\text{for the liquid phase})$$

The distribution law gives a number of equations of the type—

$$c_1 = k_1 p_1 \quad c_2 = k_2 p_2 \quad c'_1 = k'_1 p'_1 \quad c'_2 = k'_2 p'_2$$

where k_1, k_2, k'_1, k'_2 are the solubility coefficients for each molecular species, which are a function of temperature alone. From the above we get finally by division—

$$K = K' \frac{k_1^{n'_1} k_2^{n'_2}}{k_1^{n_1} k_2^{n_2}}$$

This result is of considerable importance. In most cases it is possible to determine the solubility of a given molecular

species in a solvent, and by means of the above relation it is possible to foretell how a number of substances will react in a given solvent, if the kind and extent of the reaction in the gaseous state is known, and *vice versa*. The same conclusion holds good if we are dealing with the distribution relations of a series of substances between two solvents. The above general theorem has been investigated by Kuriloff (*Zeitsch. physik. Chem.*, 25, 419, 1898).

GAS-SOLID SYSTEMS.

The simplest type of gas-solid heterogeneous equilibrium is furnished by the phenomenon of sublimation, which is exactly analogous to the process of vaporisation, and just as in this latter case the equilibrium corresponds to the setting up of a constant vapour pressure at any given temperature, the pressure being independent of the mass or volume of the system provided some solid still remains as such.

Another type which may also be regarded as belonging to a similar category is the vapour-solid equilibrium of salts containing water of crystallisation, *e.g.* $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The vapour consists of H_2O molecules, and at a given temperature there is a constant pressure, as one would expect, since the active mass of the solid¹ is constant.

The classic example of a gas-solid equilibrium which involves a distinct chemical reaction, is the dissociation of CaCO_3 into lime and CO_2 —



At any given fairly high temperature there is a definite equilibrium established, the existence of which is shown by the constancy of the CO_2 pressure. That this constancy is to be expected may be shown as follows.

In the gas phase there are some undissociated CaCO_3 molecules, some CaO molecules, and a very large number of CO_2

¹ The solid is heterogeneous, consisting of two salts, in the above case the penta- and trihydrate.

molecules. The reaction stated applies to this phase. The law of mass action therefore leads to the relation—

$$\frac{C_{\text{CaO}} \times C_{\text{CO}_2}}{C_{\text{CaCO}_3}} = \text{a constant at constant temperature}$$

But the presence of *solid* CaCO_3 and CaO , as we have already seen, means that the active mass, *i.e.* the concentration or partial pressure, of each of these is constant, and therefore the above expression becomes $C_{\text{CO}_2} = \text{constant}$ at constant temperature, or $p_{\text{CO}_2} = \text{constant}$. This has been found to be the case. The following are a few of Le Chatelier's¹ values for p_{CO_2} in the above system given for the sake of showing the magnitude of the equilibrium pressure of CO_2 at various temperatures.

$t^\circ \text{C.}$	547°.	740°.	810°.	865°.
p_{CO_2} in mm. of mercury	27	255	678	1333

On adding CO_2 to the above system at constant volume the "degree of dissociation" will be thrown back just as in homogeneous systems, *i.e.* some CaCO_3 will be formed, and since the system is saturated with respect to this it will separate out as a solid. Of course, if CO_2 at the equilibrium pressure be brought into contact with the $\text{CaCO}_3\text{—CaO—CO}_2$ system by simply making connection to another vessel containing the CO_2 gas, there will be no chemical effect produced in the system. Further, if one brings CO_2 at *less* than the equilibrium dissociation pressure into contact with *lime* alone *no* carbonate will be formed. The addition of solid CaCO_3 or CaO to the equilibrium system $\text{CaCO}_3\text{—CaO—CO}_2$ will not have any chemical effect, since the active mass of the solid is independent of its total mass, and no further CO_2 , for example, is produced by adding some more solid carbonate or lime. (Of course, if one had started with a small quantity of carbonate in a large space and raised the system to an exceedingly high temperature, the dissociation might go on until no more *solid* CaCO_3 were left, though there would

¹ Le Chatelier (*Compt. Rend.*, **102**, 1243, 1886).

always be some CaCO_3 gaseous molecules in existence, since dissociation is never absolutely complete although it may be made practically so. In such a case the active mass of the CaCO_3 is no longer constant—there being no solid—and introduction of some solid will cause a further dissociation to take place, *i.e.* more CO_2 will be formed until the equilibrium is again established. As long, however, as any solid CaCO_3 is present the same CO_2 pressure will manifest itself at a given temperature.)

Now consider another familiar case—the dissociation of solid ammonium hydrosulphide. It is supposed to take place according to the reaction—



If this is so, then on applying the law of mass action we get—

$$\frac{p_{\text{NH}_3} \times p_{\text{H}_2\text{S}}}{p_{\text{NH}_4\text{HS}}} = \text{a constant}$$

or, since $p_{\text{NH}_4\text{HS}}$ is constant as long as there is solid in the system, it follows that—

$$p_{\text{NH}_3} \times p_{\text{H}_2\text{S}} = \text{a constant}$$

This has been experimentally proved by Isambert (*Compt. Rend.*, **92**, 919, 1881; **93**, 731, 1881; **94**, 958, 1882), by adding some NH_3 or H_2S to the system and noting the final equilibrium state reached (at a given temperature)—

$p_{(\text{NH}_3)}$	$p_{(\text{H}_2\text{S})}$	$p_{\text{NH}_3} \times p_{\text{H}_2\text{S}}$
208 mm.	294 mm.	61,152
138 "	450 "	63,204
417 "	146 "	60,882
452 "	143 "	64,779

When no excess of either component had been added the *total* pressure P was observed to be 501 mm. at 25.1° . Since equimolecular quantities of each gas are produced, it follows

that one half of the observed pressure, namely 250.5 mm., is due to each gas. That is—

$$p_{\text{NH}_3} \times p_{\text{H}_2\text{S}} = \frac{P^2}{4} = (250.5)^2 = 62,750$$

which agrees well with the above constant.

On adding excess solid NH_4HS to the system which already contains some solid in equilibrium with the gases, no effect is produced for the reasons already given in the analogous case of CaCO_3 . On adding NH_3 or H_2S the dissociation is thrown back, and since each of these enters into the equation to the same degree it is immaterial which we add. Some undissociated NH_4HS is formed which comes out as solid. As long as the temperature is constant, however, the equilibrium constant is the same, that is $p_{\text{NH}_3} \times p_{\text{H}_2\text{S}} = \text{constant}$, as Isambert's experiments show. Of course the actual concentration (or partial pressure) of the gaseous components NH_3 or H_2S is altered by the addition of *one* of them, as necessarily follows in order that their product may be constant, but while the product is constant the total pressure is in this case not constant. On adding some H_2S (say) the total pressure increases, although $(p_{\text{NH}_3} \times p_{\text{H}_2\text{S}})$ remained constant. Now what is the effect of compressing the system at constant temperature?

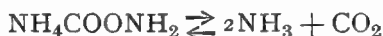
If solid NH_4HS is present the effect is nil. Some NH_3 and H_2S unite to form some solid NH_4HS , leaving at all stages of the compression the value $(p_{\text{NH}_3} \times p_{\text{H}_2\text{S}})$ constant, and since $p_{\text{NH}_3} = p_{\text{H}_2\text{S}}$ the total pressure is likewise constant. If the temperature and volume of the system are such that no solid NH_4HS is present, we can no longer regard $p_{\text{NH}_4\text{HS}}$ as constant, but must consider the whole expression—

$$\frac{p_{\text{NH}_3} \times p_{\text{HS}}}{p_{\text{NH}_4\text{HS}}} = \text{constant}$$

If such a homogeneous system be compressed at constant temperature a certain amount of NH_4HS will be formed, that is, the partial pressures of all these components will increase in such a way as to make the above expression constant.

Neither the total pressure nor the product $p_{\text{NH}_3} \times p_{\text{H}_2\text{S}}$ is in this case constant until we reach the point at which solid NH_4HS is formed, from which stage the product $p_{\text{NH}_3} \times p_{\text{H}_2\text{S}}$ is constant, and since there is not excess of any component the total pressure must be likewise constant on further diminishing the volume.

Another example, which has the historical interest of having been the first case of dissociation of solids to which Horstmann, in 1877, applied the law of mass action, is the decomposition of solid ammonium carbamate.



The dissociation is very nearly complete at moderate temperatures, that is $p_{\text{NH}_4\text{COONH}_2}$ is small compared to p_{NH_3} and p_{CO_2} .

The law of mass action gives the relation :

$$\frac{p_{\text{NH}_3}^2 \times p_{\text{CO}_2}}{p_{\text{NH}_4\text{COONH}_2}} = \text{a constant at constant temperature}$$

As long as solid carbamate exists in the system its partial pressure is constant, that is

$$p_{\text{NH}_3}^2 \times p_{\text{CO}_2} = \text{constant}$$

When no excess of either gas has been introduced it is evident that if P is the total pressure the NH_3 pressure is $\frac{2}{3}P$ and that of CO_2 is $\frac{P}{3}$, since there are twice as many NH_3 molecules produced as CO_2 molecules. The equilibrium expression, therefore, may be put in the form—

$$\frac{4P^2}{9} \times \frac{P}{3} = \frac{4P^3}{27} = \text{constant}$$

(If excess of either gas be added the ratios of the partial pressures are no longer 2 : 1 ; but in any case as long as solid is present,

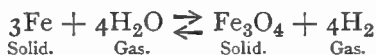
$$p_{\text{NH}_3}^2 \times p_{\text{CO}_2} \text{ is constant})$$

It will be seen that this case differs from the NH_4HS case, since one of the gaseous components is raised to a higher power

than the other. Addition of NH_3 in this case has, therefore, a greater effect in throwing back the dissociation than has addition of CO_2 .

When the system is such that no solid carbamate is present the relations are more striking. We have already considered it as an instance of homogeneous equilibrium. It was then shown that under this condition addition of NH_3 has no effect on the extent of dissociation, while CO_2 causes dissociation provided the *volume* is kept constant.

An interesting example of "double decomposition" occurs in the action of steam on iron according to the equation



The equilibrium equation is—

$$\frac{p_{\text{Fe}_3\text{O}_4} \times p_{\text{H}_2}^4}{p_{\text{Fe}}^3 \times p_{\text{H}_2\text{O}}^4} = \text{a constant at constant temperature}$$

Since Fe_3O_4 and Fe are solids, and therefore constant as regards their active mass, the equation reduces to

$$\frac{p_{\text{H}_2}^4}{p_{\text{H}_2\text{O}}^4} = \text{constant, or } \frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} = \text{constant.}$$

This is borne out by the following results :—

Temp.	p_{H_2} .	$p_{\text{H}_2\text{O}}$.	$\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}$.
{ 200	4.6	95.9	0.048}
{ 200	9.7	195.3	0.049}
{ 440	4.6	25.8	0.178}
{ 440	10.1	57.9	0.174}

Excess of one or other of the products is added in order to investigate the validity of the theoretical expression.

At about 1500°C . the ratio $\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}$ is unity, and hence, if

H_2 and H_2O vapour at the same partial pressure be passed over Fe or Fe_3O_4 , no chemical change takes place.

Other instances of gas-solid equilibria will be discussed later from the standpoint of the affinity relations involved (Part II. (Vol. II.), Chap. XI.).

An important case still remains to be mentioned, namely, the anomalies exhibited by ammonium chloride vapour.

Pressure of Dry and Moist Ammonium Chloride Vapour.—

The vapour pressure (due to sublimation) of absolutely dry solid ammonium chloride was shown by H. B. Baker to have the same value as the vapour of *moist* ammonium chloride, although in the latter case considerable dissociation of the vapour occurred while *no* dissociation is detectable when the vapour is absolutely dry. Baker's experimental conclusions were confirmed by F. M. G. Johnson (*Zeitsch. physik. Chem.*, **61**, 458, 1908). This result is quite unexpected, and even at the present time it still remains unexplained. That there is an abnormality here was first pointed out by Abegg. According to views put forward above, the concentration of the undissociated vapour ought, at constant temperature, to be independent of the presence of other gases, and therefore independent of the products of dissociation if and when such exist at the same time. Now when the AmCl vapour is moist it is known that the dissociation into HCl and NH_3 is very great, so that the concentration of the undissociated NH_4Cl molecules in the vapour must be small. One would expect, therefore, that the vapour pressure of the *dry* NH_4Cl , since it only consists of undissociated molecules, would be very small likewise. Such is not the case. A considerable discussion of this point has taken place between Abegg and van Laar (see *Chem. Soc. Reports*, **V.**, 1908, pp. 24, 25). Wegscheider's view that solid ammonium chloride can exist in two allotropic modifications, according as to whether moisture is present or not, seems to fit the facts best, though it appears at the same time a little artificial.

SOLID-SOLID SYSTEMS.

The equilibria met with in heterogeneous systems containing solids only are known as phase equilibria, analogous to the equilibrium between ice and liquid water, and are taken account of in the Phase Rule, which will be discussed later. Owing to the existence of solids the active mass of all the substances present are constant, so that the idea of a mass action equilibrium being brought about has no longer its usual significance. Such systems are characterised by possessing one or more transition points or temperatures at which the various solids are in equilibrium, but above or below which one phase *completely* disappears. This is quite different from a shift in the equilibrium point or a shift in the equilibrium constant, with temperature such as occurs in gaseous mixtures or solutions. (In solid solutions, however, reactions both homogeneous and heterogeneous can proceed, though so exceedingly slowly at ordinary temperatures that it is impossible to follow them, as can be done, for example, in the case of liquid solutions.) At the transition point referred to above with immiscible solids, the equilibrium is not a mass action equilibrium, since the equilibrium point is unaltered on addition of any of the substances present. Solid-solid equilibria are essentially instances of phase equilibria and will be considered from the standpoint of the Phase Rule.

SOLID-LIQUID SYSTEMS.

The simplest type of equilibrium in such systems—analogueous to vaporisation and sublimation—is that of the solubility of a solid in a liquid. From the kinetic standpoint equilibrium is reached when the number of molecules passing from the solid into the solution in a given time is equal to the number passing in the opposite sense. The equilibrium might be regarded as a distributional one in which the active mass of the solid is a constant, and hence its limiting concentration or *solubility* must have a certain value in a certain solvent at constant temperature.

As we have employed the saturated vapour pressure of a substance as a measure of the active mass of the substance, so we can likewise employ its solubility for the same purpose.

Let us consider one or two examples. To start with, we can take the well-known reaction in which a very soluble substance (K_2SO_4) reacts with a sparingly soluble substance ($BaCO_3$), represented by the stoichiometric equation :

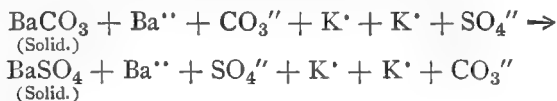


Barium sulphate and barium carbonate are only slightly soluble in water, and since their concentrations must be, therefore, very small, we assume in accordance with the theory of electrolytic dissociation that the dissociation of the small quantity in solution is practically complete. In the reaction in which we start with $BaCO_3$ and K_2SO_4 we know that some (insoluble) $BaSO_4$ is formed and an equivalent quantity of K_2CO_3 . Let us suppose that the potassium salts are also nearly completely dissociated at the concentrations at which they occur. The reaction might be represented thus :—

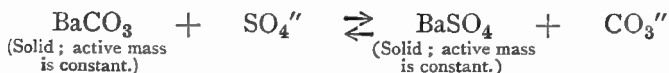


The presence of the K^* may be left out of account, for it occurs to the same extent on both sides of the equation, since K_2CO_3 (which is formed) is a similar salt to K_2SO_4 , and we know that such alkali salts are largely and equally dissociated at the same order of dilution. This, of course, has only a bearing upon the problem if the equilibrium point finally reached corresponds to the point where the concentrations of both alkali salts are nearly equal. Such happens to be the case in this reaction. The above equation, however, might be slightly misleading in the sense that in the actual mechanism of the process we do not suppose that SO_4'' acts directly upon the solid $BaCO_3$, but comes into contact with the saturated solution of the $BaCO_3$, which we have already considered as being completely dissociated into Ba^{**} and CO_3'' .

The reaction might therefore be represented thus :



Some solid BaCO_3 has disappeared and given rise to some solid BaSO_4 . This means that some K_2SO_4 has been transformed into K_2CO_3 . In other words, some SO_4'' has disappeared from solution and CO_3'' has taken its place. From the reaction



the equilibrium equation should require that

$$\frac{[\text{CO}_3'']}{[\text{SO}_4'']} = \text{constant}$$

no matter what may be the original composition of the initial mixture. To test the applicability of the law of mass action we might, therefore, start with K_2SO_4 solutions of different concentrations containing some solid BaCO_3 , and on allowing equilibrium to be set up—which at low temperatures requires months or even years—the resulting ratio $\frac{[\text{CO}_3'']}{[\text{SO}_4'']}$ determined analytically, should be the same in all cases. The results are as follows:—

Original concentration of SO_4'' (identical with original K_2SO_4 concentration).	Initial concentration of CO_3'' .	Equilibrium concentration.		$\frac{[\text{CO}_3'']}{[\text{SO}_4'']}$
		SO_4'' .	CO_3'' .	
0.0	3.5	0.719	2.781	3.9
0.0	2.0	0.395	1.605	4.1
0.0	1.0	0.176	0.824	4.6
0.25	3.8	0.843	3.207	3.8
0.25	3.0	0.658	2.592	3.9
0.50	2.0	0.50	2.0	4.0

In all the experiments quoted some K_2CO_3 was present to start with. The zero values for the SO_4'' concentration in the first three cases simply denotes that the equilibrium was being approached from the side $[\text{K}_2\text{CO}_3 \text{ solution in contact with solid } \text{BaSO}_4]$. The fact that the final values are independent of the initial conditions is evidence that a true equilibrium point was reached.

In the reaction equation given we have treated the solids BaCO_3 and BaSO_4 as possessing constant active mass. This is correct, but as we shall see later in discussing the "solubility product" or "ionic product," the assumption of constant active mass does not *in general* necessarily mean corresponding constancy of the *total* solubility (*i.e.* molecules + ions) of each solid. The solubility of all salts is affected by the presence of a common ion introduced into the system, say as a constituent of some other electrolyte. This is particularly true of such sparingly soluble substances as BaSO_4 and BaCO_3 . Thus the concentration, *i.e.* the solubility, of BaCO_3 , for example, is not the same in a solution of K_2CO_3 as it is in pure water. The active mass of the solid is, however, constant. Although the total solubility (molecules + ions) differs in the two conditions, the solubility of the molecules alone is constant,¹ and therefore in such cases it is necessary *either* to employ the term "solubility of undissociated molecules," as the true measure of the active mass of the solid, *or* to regard the square root of the solubility product (ionic product) as the correct measure. This latter view is more in accord with the mechanism of reactions in general, especially if the reacting substances are electrolytes, and are capable of giving rise to ions which react. We therefore expect that in such cases the active mass must be some direct function of the concentrations of the ions. As a matter of fact, it will be shown from the application of thermodynamics, that it is immaterial which term we choose as a measure of the active mass, *i.e.* whether we choose the concentration of the undissociated part, or the square root of the ionic product, as they are connected quantitatively the one with the other.

Although we have spoken of BaSO_4 and BaCO_3 as being so sparingly soluble that the dissolved part is *completely* dissociated, this is not absolutely correct, since there must always be undissociated molecules present (though in these cases to an extremely minute extent) in equilibrium with the ions.

The question of solubility product or ionic product will be taken up later.

¹ When the solids are very sparingly soluble.

In the reaction just considered it will be noted that owing to the slight solubility of BaSO_4 and BaCO_3 , we can neglect the quantity of SO_4'' ion or CO_3'' produced by these compared to the concentration of these ions produced by the alkali salts. Hence we can write in the above table the initial concentration of SO_4'' ion as zero in the first three cases, compared with the quantity ultimately formed in the production of K_2SO_4 . Strictly, of course, the initial concentration of SO_4'' was identical with the solubility of BaSO_4 , the dissolved portion of which is practically completely dissociated. For the same reason we can neglect any variation in SO_4'' or CO_3'' due simply to change in solubility of the barium salts. Hence the justification of simplifying the mass action expression down to the ratio $\frac{[\text{CO}_3'']}{[\text{SO}_4'']}$ derived practically entirely from the alkali salts, as a sufficient criterion of the equilibrium point of the whole reaction.

If we wish to treat the above case somewhat more accurately, we can allow for the degree of dissociation ($\alpha_1\alpha_2$) of the alkali salts by writing—

$$\frac{[\text{CO}_3'']}{[\text{SO}_4'']} \text{ as } \frac{\alpha_1[\text{K}_2\text{CO}_3]}{\alpha_2[\text{K}_2\text{SO}_4]} = \text{constant}$$

We may also look at the same reaction from a slightly different standpoint.

Suppose we start with a solution containing only K_2CO_3 and K_2SO_4 . Further, let us suppose that there is too much CO_3'' present to give the value of the ratio $\frac{[\text{CO}_3'']}{[\text{SO}_4'']}$ which it possesses when the BaCO_3 , K_2SO_4 , system is in equilibrium. Let us add a small quantity of a soluble barium salt (*e.g.* the chloride). BaCO_3 alone will be formed and precipitated in order to bring down the ratio $\frac{[\text{CO}_3'']}{[\text{SO}_4'']}$ towards the value indicated.

Similarly, if there had been too much SO_4'' , we would have had pure BaSO_4 precipitated in order to make the ratio approach the equilibrium value. Suppose that—in either case—the addition of a soluble barium salt is continued until the

$\frac{[\text{CO}_3'']}{[\text{SO}_4'']}$ has attained the equilibrium value—a process which will involve the precipitation of one single salt or the other—then at this point, on adding further soluble barium salt, both BaCO_3 and BaSO_4 will begin to come down in equivalent proportions, always keeping the ionic ratio $\text{CO}_3'' : \text{SO}_4''$ constant. It will be noted, therefore, that it is not necessarily the most insoluble salt which is precipitated first as was formerly supposed. Which salt is precipitated depends on the relative concentration values of the ions which determine the equilibrium. We might represent the behaviour diagrammatically thus (Fig. 32)—

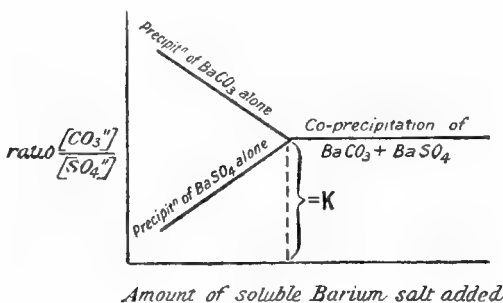


FIG. 32.

The same behaviour was observed by Findlay (*Zeitsch. physik. Chem.*, **34**, 409, 1900) in connection with the reaction—



in which evidently the equilibrium is determined by the equation—

$$\frac{[\text{SO}_4'']}{[\text{I}']^2} = K$$

The Solubility Product or Ionic Product (Elementary Treatment).—For the introduction of this important conception into heterogeneous electrolytic equilibrium we are indebted to Nernst (*Zeitsch. physik. Chem.*, **4**, 372, 1889). We are familiar with the application of the law of mass action in the

form of Ostwald's dilution law to the electrolytic dissociation of water itself, namely—



the equation taking the form—

$$\frac{C_{\text{H}'} \times C_{\text{OH}'}}{C_{\text{H}_2\text{O}}} = \text{constant}$$

or, since the concentration of the water is constant, $C_{\text{H}'} \times C_{\text{OH}'} = \text{constant}$. This constant may be called the "ionic product" as well as ionisation constant. In the case of saturated solutions of electrolytes in which some solid is present, the idea of distribution, as we have seen, would lead to an equilibrium being set up when there is equality in the number of molecules passing in opposite directions to and from the solid. The ratio of the concentration in the two phases is constant at the equilibrium point by definition, and since the "concentration" in the solid is constant, the concentration of molecules in solution is constant as long as we can regard the solvent as the same, *i.e.* as long as it is unmodified by the presence of the ions themselves. It will be noted that we are dealing with the distribution of the same kind of molecular species as is necessary in accordance with Nernst's definition of the distribution law.

Now let us consider the application of the law of mass action to the dissolved state, *i.e.* the ions and molecules. If we are dealing with a simple binary dissociation such as that of AgCl into Ag' and Cl', we have the relation—

$$\frac{[\text{Ag}'][\text{Cl}']}{[\text{AgCl}]} = \text{constant}$$

supposing the simple form of the law of mass action, *i.e.* the dilution law, to hold good. But we have just seen that in the saturated state [AgCl] is constant—

$$\therefore [\text{Ag}'][\text{Cl}'] = \text{a constant}$$

called the SOLUBILITY PRODUCT or IONIC PRODUCT. This is of fundamental importance in dealing with solubility relations of electrolytes especially of sparingly soluble salts. It will be seen from the above that if we increase the concentration

of either ion, the other ion will decrease in concentration in order to keep the concentration product constant. Thus if we add KCl to AgCl saturated, the Ag^+ must decrease in concentration. It can only do so by forming some undissociated AgCl. But the solution is saturated, and in accordance with the distribution or partition law, the concentration of AgCl (undissociated) is constant, and hence some of the undissociated AgCl is precipitated in the solid form. The total solubility of AgCl is therefore less in presence of KCl than it is in pure water. At the same time it is important to note that the concentration (solubility) of the undissociated molecules is the same whether KCl is present or not, provided KCl is not in such quantity as to alter the nature of the solvent. It is evidently in accordance with the idea of the active mass of the solid being constant no matter what substances may be introduced into the liquid in contact with it. The conclusion that the dissolved undissociated molecules possess a constant concentration having a certain numerical value, holds, of course, only as long as we keep to the same solvent. It might be possible to add so much extraneous material, *e.g.* alcohol, say, to an aqueous solution of saturated AgCl, as to alter the concentration of the dissolved undissociated AgCl molecules. This would appear to be in contradiction to the idea of the solid AgCl having a constant active mass. It must be remembered, however, that a proportionality, and not an identity exists between the active mass of a solid, and the concentration of undissociated dissolved molecules. The proportionality further varies with the *nature* of the solvent, but is independent of the chemical nature of the solid, which is partially dissolved.¹ (This, of course, assumes that no specific chemical action comes in between solid and solvent, as in the case of Na in contact with water.) In the cases here considered the dissociation is supposed so great that we only take ions into consideration. To return to the case of the saturated aqueous solution of silver chloride. In the presence of KCl or other electrolyte having an ion in common

¹ This, of course, does not mean that all salts have the same solubility in a given solvent, for salts have different active masses.

with one or other of the ions of the sparingly soluble body, its solubility is said to be decreased. This statement is true if we are referring to the concentration of the ion, which has *not* been increased by addition of a soluble electrolyte (KCl). In pure water AgCl dissolves slightly, giving rise to a quantity of Ag^+ and Cl' , which are evidently present in equivalent amounts. The solution might be looked upon as symmetrical with respect to the ions. The ionic product has a certain value, L_0 . On adding KCl, some solid AgCl is precipitated. The Cl' is increased, the Ag^+ is correspondingly decreased in such a way as to make $[\text{Ag}^+][\text{Cl}'] = L_0$, as before. The solution is now asymmetric with respect to the Ag^+ and Cl' . In speaking of solubility in such a case we fix our attention on the amount of Ag and Cl in equivalent proportions, which still remain in the solution, and could be withdrawn from it. That is, we fix our attention on the ion least represented. In the case of AgCl in presence of KCl, the Ag^+ ion is evidently the ion least represented. The solubility of a sparingly soluble electrolyte in presence of soluble electrolyte with a common ion is evidently a more composite term than the solubility of an electrolyte (or non-electrolyte) in the solvent alone. Again, as already pointed out, the saturated solution of a body such as AgCl is very dilute, and since it is a salt, the small quantity which is dissolved suffers almost complete dissociation in solution. Hence the concentration of the undissociated molecules must be small compared even to that of the ions. That is, C_0 is negligible compared to the concentration $[\text{Ag}^+]$ or $[\text{Cl}']$. Hence in such a case, say when AgCl is dissolved in water alone, the concentration of Ag^+ or of Cl' in gram ions per liter gives a number identical with the solubility of the entire salt. But $[\text{Ag}^+] \times [\text{Cl}'] = L_0$. Hence the solubility is identical with the $\sqrt{\text{solubility product}}$. Now take the case of AgCl in presence of some KCl. The solubility simply becomes identical with the concentration of the least represented ion, *i.e.* the Ag^+ ion. An estimation of the Ag^+ ion in solution is therefore the experimental way of arriving at the solubility of AgCl in aqueous KCl solution. We can evidently calculate this quantity if we know what

value L_0 has—say by estimating the Ag^+ or Cl' in *absence* of KCl —and remembering that L_0 is constant whether KCl is present or not. By the addition of the KCl in a given amount we know the quantity of Cl' present (the Cl' originally present from the AgCl itself being usually negligible compared to the quantity thus added), and the “solubility” of the AgCl in presence of KCl , or the Ag^+ concentration is simply—

$$(\text{Ag}^+) = \frac{L_0}{[\text{Cl}']}$$

More frequently, as a matter of fact, one employs the ionic product to calculate the solubility of a salt such as AgCl in water alone from data obtained when KCl is present. In the latter case an easy method of determining the Ag^+ ion present in a known quantity of KCl (known Cl' ion concentration) is afforded by electromotive measurements to which we shall come in dealing with the subject of electro-chemistry. Having determined the Ag^+ concentration in such a case and knowing the Cl' concentration, the product of the two gives the solubility product, L_0 . When AgCl is dissolved in water alone we have seen—assuming practically complete dissociation—that the solubility (which is now symmetrical in respect to each ion) is simply $\sqrt{L_0}$, and hence the solubility may be easily obtained without an actual determination in pure water—an operation of considerable difficulty.

By way of showing that the addition of a common ion to a saturated solution of an electrolyte causes the remaining ion or ions to diminish in concentration in accordance with the expression $\frac{[\text{cation}][\text{anion}]}{[\text{undissociated electrolyte}]} = \text{a constant}$, one may quote the following figures given by Nernst (*Zeitsch. physik. Chem.*, 4, 379, 1889):—

Solubility of silver acetate in gram-molecules per liter (aqueous solution).	Concentration of added sodium acetate.
0.0603	0
0.0392	0.061
0.0282	0.119
0.0208	0.230

Solubility of silver acetate.	Concentration of silver nitrate added.
0.0603	0
0.0417	0.061
0.0341	0.119
0.0195	0.230

The solubility of silver acetate decreases with increasing concentration of either sodium acetate or silver nitrate, and for equivalent amounts of each the solubility is approximately equally reduced.

PRECIPITATE FORMATION AND THE METHODS OF ANALYTICAL CHEMISTRY.

We are now in a position to understand the conditions which determine the formation or non-formation of a precipitate by the interaction of ions.

A sparingly soluble electrolyte—acid, salt, or base—will be precipitated from solution when the product of the concentrations of the ions present exceeds a certain value, viz. the solubility product. The principles are quite the same for the three kinds of electrolytes named, but the most important case for our present purpose is that of the formation of salts which are only slightly soluble in the solvent.

If we bring AgNO_3 and KCl together in a solution so dilute that the product $[\text{Ag}'] \times [\text{Cl}']$ is less than the solubility product L_0 for the given salt (AgCl) in the particular solvent, then no precipitate is formed. This in practice is rare, because L_0 for this salt is extremely small.

What has been said for AgCl holds, of course, equally well for numerous other cases. AgI has a much smaller solubility and therefore much smaller solubility product than AgCl . The question now arises—what is the effect of adding KI solution to some AgCl , and how far will the reaction



proceed ?

When equilibrium is reached we know that the law of the ionic or solubility product must be satisfied for the saturated solution of each of the bodies AgCl and AgI . That is, the conditions to be satisfied are—

$$\begin{cases} [\text{Ag}'] \times [\text{Cl}'] = L_{\text{AgCl}} \\ [\text{Ag}'] \times [\text{I}'] = L_{\text{AgI}} \end{cases}$$

$$\therefore \frac{[\text{Cl}']}{[\text{I}']} = \frac{L_{\text{AgCl}}}{L_{\text{AgI}}} = \text{a constant, } K$$

That is to say, the reaction goes on until the ratio of the $\text{Cl}' : \text{I}'$ is the same as the ratio of the solubility or ionic products of the sparingly soluble salts. Now according to measurements of Goodwin (*Zeitsch. phys. Chem.*, **13**, 588, 1894),

$$L_{\text{AgCl}} = 1.56 \times 10^{-10},$$

i.e. the solubility of AgCl in water is $\sqrt{1.56 \times 10^{-10}}$,

and

$$L_{\text{AgI}} = 0.94 \times 10^{-16}$$

\therefore the ratio is 1.6×10^6 . That is to say, the reaction proceeds until the Cl' concentration becomes over one million times greater than the I' concentration. *Practically*, therefore, all the AgCl originally present is transformed into AgI .

We may now consider a simple instance of the applicability of the theory of ions and ionic product to a quantitative volumetric method, namely, to Mohr's method of estimating the chlorine content in a soluble chloride by titration with AgNO_3 , using potassium chromate (K_2CrO_4) as indicator. Ag_2CrO_4 is much *more* soluble, *i.e.* has a greater solubility product than AgCl in the ratio of $2.89 \times 10^{-8} : 1.56 \times 10^{-10}$. Hence, on adding AgNO_3 to a solution containing CrO_4'' , before the solubility product of Ag_2CrO_4 can be reached, that is to say before any precipitation of this salt can take place, the concentration of CrO_4'' must be 200 times greater than the concentration of Cl' . Now only a very little CrO_4'' is added (a drop or two of K_2CrO_4 solution) to the KCl solution, and hence when AgNO_3 is run in from the burette the result will be that Cl' will first be removed (as AgCl precipitate) until the Cl' is reduced in concentration to $\frac{1}{200}$ th of the CrO_4'' ion. This means that practically no Cl' ion is in solution at all when the

stage is arrived at at which the solubility product of Ag_2CrO_4 is reached. That is to say, practically all the chloride originally present (as KCl) has been converted into AgCl , and from the quantity of standard AgNO_3 run in it is easy to calculate the chlorine ion originally present.

A further illustration of similar principles is to be found in the ordinary method of qualitative separation of metals by H_2S in acid and alkaline solution. H_2S is a weak acid, *i.e.* it gives rise to a small number of ions which we can for the moment regard as H^+ and S'' . If we add HCl to the H_2S solution we still further throw back the concentration of S'' ion, for we have increased the H^+ and we know that $\frac{[\text{H}^+]^2[\text{S}'']}{[\text{H}_2\text{S}]}$ must be constant. Now it happens to be the case that the sulphides of the metals As , Sb , Sn , Pb , Cu , Hg , Bi , Cd are extremely insoluble, their solubility products being extremely small. These metals may be referred to as 1st Group. On the other hand, the sulphides of the metals of Group II, Ni , Co , Zn , Mn , Fe , are more soluble than those of the 1st Group. If a solution contains metals of both groups and an acidified solution of H_2S is added, the system then contains a very small quantity of S'' ions. In the case of the 1st Group metals, even this small quantity of S'' ions is such that the concentration values of S'' and metal⁺⁺ exceeds the ionic product of the corresponding metallic sulphide, and hence precipitation of these sulphides takes place. The concentration of S'' is, however, too small to precipitate the 2nd Group metals, for the product of the S'' ions \times metal ion⁺⁺ is less than the solubility product of the sulphides of the 2nd Group. In order to bring down the sulphides of the 2nd Group it is necessary to add a considerable quantity of S'' ions. This is done not by adding the weakly dissociated acid H_2S , but by adding a soluble sulphide, *e.g.* $(\text{NH}_4)_2\text{S}$, which being a salt is largely dissociated in solution, and hence it is conceivable that the point may be reached when the product of S'' ion and the metal ion of the 2nd Group now exceeds the solubility product of the sulphide and precipitation occurs. (It is obvious that $(\text{NH}_4)_2\text{S}$ will even more completely precipitate the 1st Group metals, but, of

course, no separation of Groups I and II could thereby be effected.)

Another important problem frequently met with is the solution of a precipitate by chemical means, *e.g.* the solution of a precipitated sulphide by an acid such as HCl. The process essentially depends on the fact that the precipitate is a salt which contains a weak constituent (anion or cation), and the reagent added must give rise to the complementary ion in large quantity. ZnS suspended in water has a certain solubility and solubility product. On adding H^+ by means of HCl, it is found that the product of the $[H^+]$ and $[S'']$ is sufficiently great that these ions cannot exist in presence of one another entirely uncombined, and hence some undissociated H_2S is formed, evidently at the expense of the ions. The S'' ion in solution tends to decrease in quantity owing to this recombination, but in order that the solubility product of the ZnS may be maintained constant, further ZnS dissolves in the ionic form. The S'' again rises to too great values, and more undissociated H_2S is formed. In this continuous process the solution is evidently becoming richer in Zn^{++} , richer in undissociated H_2S , and the mass of ZnS precipitate decreases. This can go on until the ZnS is completely dissolved. If we had started with a limited quantity of strong HCl solution, it is clear that the solubility of H_2S in the solution might easily have been exceeded, and since this happens to be a gaseous body it will be evolved as such. It will be observed that the ratio of the values of the solubility product of the metallic sulphide and of the dissociation constant of H_2S is of great importance in determining whether the sulphide will dissolve in a given acid, *i.e.* in presence of a given H^+ ion concentration or not. Thus take a sulphide such as HgS , which is the most sparingly soluble one known, and add some dilute HCl to a suspension of the sulphide in water. As before we have H^+ and S'' present together in the solution, but now, owing to the extremely small quantity of S'' present from the sulphide, the product of the H^+ and S'' is so small that practically there is no union of these to form undissociated H_2S , and hence the metallic sulphide only dissolves to an infinitesimal amount.

To get any considerable quantity to dissolve we have to increase the H^+ as much as possible, and raise the temperature of the system, since the solubility of most solids in liquids increases with a rise of temperature, and even then the solution of the sulphide may not be complete, for evidently the H^+ becomes used up partially in the process to form undissociated H_2S , and at a certain stage the H^+ ion may become too low in value to unite further with the S'' , *i.e.* to cause further solution of the metallic sulphide. Of course the fact that actually *precipitation* of sulphides of 1st Group metals can take place in moderately acid solution of H_2S shows that in such a case the H^+ is too small to cause the reverse process, *i.e.* solution of sulphide in presence of the exceedingly small S'' , the smallness being due to the small solubility of the metallic sulphide formed. CdS is the most soluble of the 1st Group of sulphides. One would expect, therefore, if we wish to get the precipitate to form, that only a very slightly acid solution is necessary, and that if one used a strong acid solution the S'' present (from the H_2S) would not be great enough to combine with the metal and form the metallic sulphide. It is, therefore, possible to precipitate CdS with H_2S in dilute HCl solution, and to redissolve it by adding more HCl . It is clear from the foregoing consideration that Group II metal sulphides will dissolve much more easily in a solution containing H^+ ion than will the metal sulphides of Group I—for the solubility and solubility product of Group II metal sulphides is much greater than those of Group I. In general, therefore, every precipitate which is not too insoluble (HgS is near the limit) and which contains a weak anion (*e.g.* carbonates, sulphides, cyanides, phosphates, oxalates, hydroxides) will dissolve in a solution which contains H^+ ions in sufficient quantity. It is clear from the above that hydroxides should dissolve in presence of H^+ ion, *i.e.* in acids even more easily than sulphides or carbonates, because the dissociation of the weak "acid" H_2O is less than any other weak acid or base, and hence in the case of an hydroxide, such as $Al(OH)_3$ in suspension in water, the OH' formed from the hydroxide in presence of even a small quantity of H^+ gives rise to an

ionic product which exceeds the ionic product or ionisation product for H_2O , and hence undissociated H_2O is progressively formed, the $\text{Al}(\text{OH})_3$ gradually dissolving in order to keep its own solubility product constant.

Hitherto we have regarded the electrolytic dissociation of H_2S as proceeding according to the equation $\text{H}_2\text{S} \rightleftharpoons 2\text{H}' + \text{S}''$. As a matter of fact, however, it takes place in two stages, each with a definite equilibrium constant, k_1 and k_2 , viz. $\text{H}_2\text{S} \rightleftharpoons \text{HS}' + \text{H}'$ and $\text{HS}' \rightleftharpoons \text{H}' + \text{S}''$. The whole question of the equilibrium conditions of the metallic sulphides in aqueous solution has been studied by the late Professor Bruner (Bruner and Zawadzki, *Bull. de l'Acad. de. Sc. de Cracovie*, July, 1909). A few illustrative examples may be quoted. In general the following relations must be satisfied when the system is in equilibrium—

$$[\text{MeS}] = \text{constant}$$

(undissociated dissolved molecules in equilibrium with the solid sulphide)

$$\begin{aligned} \text{MeS} &\rightleftharpoons \text{Me}'' + \text{S}'' \\ k[\text{MeS}] &= [\text{Me}'] \times [\text{S}'] \\ \text{H}_2\text{S} &\rightleftharpoons \text{H}' + \text{HS}' \\ \text{HS} &\rightleftharpoons \text{H}' + \text{S}'' \\ k_1[\text{H}_2\text{S}] &= [\text{H}'] \times [\text{HS}'] \\ k_2[\text{HS}'] &= [\text{H}'] \times [\text{S}'] \\ \therefore [\text{S}'] &= k_1 k_2 \frac{[\text{H}_2\text{S}]}{[\text{H}']^2} \\ \therefore k[\text{MeS}] &= k_1 k_2 [\text{Me}'] \frac{[\text{H}_2\text{S}]}{[\text{H}']^2} \\ \therefore \frac{k}{k_1 k_2} [\text{MeS}] &= \frac{[\text{Me}'] [\text{H}_2\text{S}]}{[\text{H}']^2} = K \quad . \quad . \quad (1) \end{aligned}$$

Equation (1) shows that when equilibrium is reached the concentration of the metal ion in the solution is inversely proportional to the concentration of the undissociated H_2S molecules, and directly proportional to the square of the concentration of the H' ion. To test the foregoing conclusions it is necessary to get a case in which a *measurable* equilibrium

point exists. Bruner considers zinc salts as unsuitable, owing to the fact that the sulphide precipitation is not a reversible process, but the requisite considerations are met with in the case of thallium.

The equilibrium $2\text{Ti}^+ + \text{H}_2\text{S} \rightleftharpoons \text{Ti}_2\text{S} + 2\text{H}^+$ at 25° was investigated, first keeping the concentration of the H_2S constant, and secondly allowing it to vary by known amounts. A moderately good equilibrium constant was obtained even when the absolute values of the concentration terms altered over a fairly wide range. This equilibrium constant K is directly proportional to the solubility product L , as may be seen from equation (1). For metals which give rise to uni-, di-, and tri-valent ions respectively, the following relations hold good. For univalent metals—

$$L_1 = [\text{Me}']^2 \times [\text{S}'''] \quad K_1 = \frac{[\text{Me}']^2 \times [\text{H}_2\text{S}]}{[\text{H}']^2}$$

For divalent metals—

$$L_2 = [\text{Me}''] \times [\text{S}'''] \quad K_2 = \frac{[\text{Me}''] [\text{H}_2\text{S}]}{[\text{H}']^2}$$

For trivalent metals—

$$L_3 = [\text{Me}''']^2 [\text{S}''']^3 \quad K_3 = \frac{[\text{Me}''']^2 [\text{H}_2\text{S}]^3}{[\text{H}']^6}$$

The sulphur ion concentration is a function of the H_2S and H^+ ion concentrations, according to the following :—

$$[\text{S}'''] = k_1 k_2 \frac{[\text{H}_2\text{S}]}{[\text{H}']^2}$$

For, according to the law of mass action, we have—

$$k_1 [\text{H}_2\text{S}] = [\text{H}'] [\text{HS}']$$

$$k_2 [\text{HS}'] = [\text{H}'] [\text{S}''']$$

and therefore $[\text{S}'''] = k_1 k_2 \frac{[\text{H}_2\text{S}]}{[\text{H}']^2} = k' \frac{[\text{H}_2\text{S}]}{[\text{H}']^2}$

The first dissociation constant k_1 of H_2S has been determined several times. Auerbach's value is 0.91×10^{-7} . The

second dissociation constant k_2 , according to Knox, is 1.2×10^{-15} . Hence $k' = 1.092 \times 10^{-22}$, and therefore—

$$L_1 = 1.092 \times 10^{-22} K_1$$

$$L_2 = 1.092 \times 10^{-22} K_2$$

$$L_3 = (1.092)^3 \times 10^{-66} K_3.$$

For thallium sulphide $L_1 = 7.0 \times 10^{-23}$ at 25°C .

A few other sulphides are taken from Bruner's table—

MeS.	K.	L.	Concentration of th metal ion when $[H] = 1(N)$ and $H_2S = 0.1$.
MnS	6.3×10^6	7×10^{-16}	—
FeS	3.4×10^3	3.7×10^{-19}	3.4×10^2
TlS	6.37×10^{-1}	7.0×10^{-23}	2.5
α ZnS	$(7.3 \text{ to } 4.5) \times 10^{-4}$	$(8.0 \text{ to } 5.0) \times 10^{-26}$	$(7.3 \text{ to } 4.5) \times 10^{-1}$
β ZnS	<i>circa</i> 10^{-2}	1.1×10^{-21}	10^{-1}
CdS (from CdCl_2)	6.5×10^{-9}	7.1×10^{-28}	6.5×10^{-5}
CdS (from CdSO_4)	4.6×10^{-7}	5.1×10^{-29}	4.6×10^{-6}
PbS	3.1×10^{-6}	3.4×10^{-28}	3.1×10^{-5}
CuS	$(5.3 \text{ to } 1.1) \times 10^{-20}$	$(5.9 \text{ to } 1.2) \times 10^{-42}$	$(5.3 \text{ to } 1.1) \times 10^{-1}$
Ag_2S	$(3.6 \text{ to } 1.35) \times 10^{-28}$	$(3.9 \text{ to } 1.47) \times 10^{-50}$	$(6.0 \text{ to } 3.7) \times 10^{-1}$
HgS	7.0×10^{-28}	7.7×10^{-48}	7.0×10^{-25}
HgS	9.0×10^{-32}	1.0×10^{-53}	9.0×10^{-31}

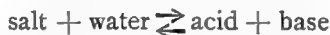
The different values obtained by different investigators is very striking. A factor of great importance is the size of the particles composing the precipitate, as it has been shown—in the case of BaSO_4 , for example—that the solubility increases as the size of the particles becomes smaller. It is evident that a considerable amount of useful work still remains to be done in this department of analytical chemistry. It should be pointed out that the relation, viz. equality between the solubility of an “insoluble” salt in water and the square root of its solubility product, only holds strictly if *hydrolysis* is negligible.

As supplementing the solubility table above, given in the case of sulphides, the following values for a few commonly occurring sparingly soluble halides and PbSO_4 are quoted. Temperature 25°C .

Salt.	Solubility in water in equivalents per liter.	Solubility product L.
AgCl . . .	1.25×10^{-3}	1.56×10^{-10}
AgBr . . .	6.6×10^{-4}	4.35×10^{-13}
AgI . . .	1.0×10^{-5}	1.0×10^{-16}
PbSO ₄ . .	1.5×10^{-3}	2.2×10^{-8}

It is evident from the foregoing considerations that a salt, such as BaSO₄, which is very sparingly soluble in water, possessing therefore an extremely small ionic product and at the same time containing acid and basic constituents which are *strong*, will not be dissolved except to an infinitesimal extent on adding even a strong acid (or a strong base). Thus, on adding acid to BaSO₄ (in suspension, say) the quantity of H⁺ which can be introduced, even as a maximum, is not great enough to cause the H⁺ and SO₄²⁻ to unite to form undissociated H₂SO₄ except to an infinitesimal extent, for this acid being a very strong one is itself largely dissociated into ions.

Heterogeneous Hydrolytic Equilibrium.—What has been said above in connection with weak anions holds equally well with regard to weak cations. We have an illustration of this in a special case of *heterogeneous hydrolytic equilibria* in which the base is weak and the acid strong, viz. diphenylamine picrate, which hydrolyses into picric acid and diphenylammonium hydroxide. This base (or, as it is usually taken to be, simply diphenylamine) is practically insoluble in water. That is to say, its active mass is constant; similarly diphenylamine picrate is insoluble, and the hydrolytic expression—



yields when the law of mass action is applied—

$$C_{\text{acid}} = \text{constant}$$

Hence, if to a hydrolysed diphenylamine picrate solution some picric acid is added, the system will so change as to retain the acid at its (original) concentration previous to the addition. This can evidently only take place by some solid diphenylamine picrate being precipitated from solution. The

system and its behaviour is exactly analogous to the CaCO_3 , CaO , CO_2 gaseous equilibrium. Notice also if in this latter system CO_2 at less than the equilibrium pressure be brought into contact with CaO no CaCO_3 is formed, so if picric acid at less than the equilibrium concentration be brought into contact with diphenylamine no picrate is formed. This can be shown by the different colour effects produced, for picric acid itself is yellow, diphenylamine is colourless, and the picrate is brown. On adding picric acid containing 14 grams per liter at 40.6°C . to the diphenylamine, the base is stained brown owing to formation of picrate. If the solution of acid contains 13 grams per liter no coloration is produced.

This startling behaviour and its dependence on the fact that the picric acid must have a constant concentration at a given temperature, should be compared with the analogous hydrolytic reaction in which picrate of urea, which is only sparingly soluble in water, hydrolyses, giving rise to urea and

picric acid. The law of mass action requires that $\frac{C_{\text{acid}} \times C_{\text{urea}}}{C_{\text{salt}} \times C_{\text{H}_2\text{O}}}$

shall be constant, or $C_{\text{urea}} \times C_{\text{picric acid}} = \text{constant}$, both of these being easily soluble in water. If we take this system and add picric acid, the result is that there is a permanent increase in picric acid concentration (compared with the initial concentration value), but at the same time some of the urea disappears from solution, having been transformed into picrate of urea, which is sparingly soluble, some of which is therefore precipitated. The case is analogous to the gaseous dissociation of solid ammonium hydrosulphide.

For further details of the above the student is referred to J. Walker and J. R. Appleyard, *Picric Acid and Diphenylamine* (*Trans. Chem. Soc.*, **69**, 1341, 1896). For heterogeneous equilibria between electrolytes in general, the student is referred to Abegg's *Theory of Electrolytic Dissociation*. Having discussed and illustrated the principle of the mutual action of ions upon one another in so far as it affects the solubility of salts, it is necessary to consider more precisely what rôle is played by the undissociated portion and how far the above generalisation is true.

RECENT WORK ON THE SOLUBILITY PRODUCT.

(Noyes and collaborators, *Journ. Amer. Chem. Soc.*, **33**, 643, 1911.)

Noyes in the introduction to the experimental investigation, which deals largely with thallium salts, states the position of the problem as follows:—

The following well-known solubility principles were originally formulated upon the basis of the law of mass action:—

I. The product of the concentration of the ions of a salt present as solid phase has the same value in dilute solutions of other salts as it has when it is present alone (Nernst, *Zeitsch. physik. Chem.*, **4**, 379, 1889).

II. The concentration of the unionised portion of a salt present as solid phase has the same value in dilute solutions of other salts as it has when present alone (A. A. Noyes, *Zeitsch. physik. Chem.*, **6**, 243, 1890).

It was, however, early recognised that both of these principles cannot hold true accurately, since the ionisation of salts (as derived from the conductance ratio $\left(\frac{\Delta_v}{\Delta_\infty}\right)$ or freezing-point lowering) does not change with the concentration in accordance with the law of mass action [*i.e.* Ostwald's dilution law does not hold]. The first principle has been generally employed, since it was shown by Arrhenius that the second of the above principles is not even approximately true (*Zeitsch. physik. Chem.*, **31**, 224, 1899). Thus Arrhenius showed that in the data obtained by Noyes for the solubility of TiCl , the solubility of the TiCl , namely (0.00170 N) in presence of 0.8 N KCl , is *less* than the undissociated part of TiCl (*viz.* 0.00179 N) when no KCl is present. Arrhenius found the same thing in connection with the solubility of silver salts of organic acids in presence of a common ion, the concentration of the unionised part decreasing rapidly with increasing concentration of the common ion, even beyond the point at which the total solubility became less than the concentration of the unionised portion in pure water. Stieglitz (*Journ. Amer. Chem. Soc.*, **30**, 946, 1908) concluded from a further study of

the same data, that the first principle expressing the constancy of the product of the ion-concentrations is approximately true for these uni-univalent¹ silver salts, and suggested that this might be adopted for the present as an approximate empirical principle. Recent computations have shown, however, that the first principle is also subject to considerable deviations, and that these lie in a direction opposite to that of the deviations from the second principle. Thus it has been computed (Noyes, *Zeitsch. physik. Chem.*, **52**, 636, 1905) that in a solution saturated at 40° C., both with thallous chloride and thallous thiocyanate, where the total concentration is about 0.04 N, the concentration of the unionised TlCl is about 15 per cent. less, and the product of the concentration of the Tl' and Cl' ions about 5 per cent. greater than it is in a solution of thallous chloride alone.

"Any such computations necessarily involve some principle in regard to the ionisation of salts in mixtures. Assuming that the conductance-ratio $\frac{\Lambda}{\Lambda_0}$ is an accurate measure of ionisation, the following principle, first stated by Arrhenius,² has been well established in the case of uni-univalent salts through the study of the conductance of mixtures of them, viz.³ in a mixture of two salts with a common ion, each salt has a degree of ionisation equal to that which it has when alone present in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture. This principle when combined with the empirical law, which has been found to express the change of the ionisation $\alpha = \frac{\Lambda}{\Lambda_0}$ of single salts, with the concentration (C)—

$$\frac{(Ca)^n}{C(1-\alpha)} = K \dots \dots (1)$$

¹ This is Noyes' nomenclature for indicating the valences of the constituent ions of salts, e.g. AgCl is a uni-univalent salt, Ag₂SO₄ is a uni-bivalent salt, PbSO₄ is a bi-bivalent salt, AlCl₃ is a tri-univalent salt, and so on.

² *Zeitsch. physik. Chem.*, **2**, 285, 1888; **31**, 218, 1899.

³ For references, see Sherrill, *Journ. Amer. Chem. Soc.*, **32**, 741, 1910.

may be expressed mathematically by the following equation¹:—

$$\frac{C_{B+}C_{A-}}{C_{BA}} = K(\Sigma C_i)^{2-n} \quad . \quad . \quad . \quad (2)$$

where K is a constant characteristic of the salt, C_{B+} and C_{A-} are the concentrations of the positive and negative ions, of a salt BA , C_{BA} that of the unionised portion of the salt, and ΣC_i denotes the sum of the equivalent concentrations of all the positive or negative ions present in the solution, a quantity which will hereafter be called the total ion-concentration. The exponent n has a value lying almost always between 1.40 and 1.60.

“In applying this equation (2) to any special mixture the values of α , ΣC_i , n and K are first determined for each salt from the conductance data for the salt, and the values of C_{B+} , C_{A-} and C_{AB} for each salt in the mixture and of ΣC_i are then computed from the equation by a method of approximation.² In mixtures with a common ion it is only necessary to know the relation between α and ΣC_i for each salt, since the above ionisation rule may then be applied directly. In mixtures without a common ion the relation of the function $\frac{C_{B+}C_{A-}}{C_{BA}}$ to ΣC_i is determined for the separate salts, and is

then applied for calculating the concentrations in the mixture.

“It is important to note that the only evidence in favour of equation (2) is that the specific conductances of mixtures calculated with its aid are in good agreement with the experimental values. It therefore will furnish correct values of the ion-concentrations only in case the commonly accepted principle is correct, that the conductance ratio $\frac{\Lambda}{\Lambda_0}$ is a reliable measure of the degree of ionisation of a single salt, a principle

¹ Arrhenius, *Zeitsch. physik. Chem.*, **31**, 218, 1899. Sherrill, *Loc. cit.*

² For examples see *Journ. Amer. Chem. Soc.*, **32**, 741, 1910; **31**, 754, 1909.

which can be true only in case the mobilities of the ions do not vary with the concentration.

"In the case of salts of the uni-bivalent type, there is, furthermore, the uncertainty as to whether intermediate ions (such as KSO_4^- or NO_3Ba^+) are present in considerable proportions."

SATURATED TlCl SOLUTIONS. SOME RESULTS.

Added salt (KCl).	($\Sigma\text{Tl.}$)	($\Sigma\text{Cl.}$)	(K^+)	(Tl^+)	(Cl^-)	($\frac{1}{2}\text{Ba}^{++}$)	($\frac{1}{2}\text{BaCl}_2$)	(KCl)	(TlCl) (undissociated salt).	($\text{Tl}^+)(\text{Cl}^-)$ (ionic product).
0.0	16.07	14.32	0.0	14.32	14.32	—	—	0.0	1.755	204.9
25.0	8.69	29.88	22.58	7.30	29.88	—	—	2.42	1.390	218.1
50.0	5.90	48.85	44.15	4.70	48.85	—	—	5.85	1.204	229.6
100.0	3.96	88.40	85.5	2.90	88.40	—	—	14.5	1.061	256.3
200.0	2.68	166.54	164.8	1.74	166.54	—	—	35.2	0.94	290.0
$\frac{1}{2}\text{BaCl}_2$ added.										
0.0	16.07	14.32	—	14.32	14.32	0.0	0.0	—	1.755	204.9
25.0	8.98	28.00	—	7.59	28.00	20.41	4.59	—	1.392	212.5
50.0	6.18	44.30	—	4.98	44.30	39.32	10.68	—	1.203	220.6
100.0	4.16	77.97	—	3.11	77.97	74.86	25.14	—	1.052	242.4
200.0	2.82	142.7	—	1.89	142.7	140.8	59.2	—	0.93	270.0

"This 'unionised' concentration and this 'solubility product' should, according to the mass action law, be constant in any saturated solution. The actual variations of these quantities in the different cases are shown in the last two columns of the table. In every case the unionised concentration (BA) *decreases* markedly and the solubility product ($\text{B}^+)(\text{A}^-)$ *increases* slightly, as the total concentrations of the salts and of the ions in the saturated solution increase."

In the case of very insoluble substances, such as the metallic sulphides of Groups I and II, and the silver halides, etc., the simple view already expounded regarding the constancy of the ionic product in presence of moderately dilute solutions (reagents) containing ions common to precipitated substance and precipitating agent, may still be regarded as

very nearly true. For further details upon the very important bearing of physico-chemical principles upon problems in analytical chemistry, the reader is referred to Wilhelm Ostwald's *Foundations of Analytical Chemistry*, translated by McGowan, or the more recent work of Stieglitz, *Elements of Qualitative Chemical Analysis*.

As regards the problem of the solubility relations of easily soluble salts in their action upon one another's solubility very little is as yet known. The difficulty is that in concentrated solutions such as are met with in these cases, it is no longer justifiable to attempt to apply relationships deduced for dilute solutions. The relation between the osmotic pressure and the concentration, for example; is no longer one simply of direct proportionality. There is a great deal of scope for investigation here. Since no wide generalisations have as yet come to light, it must suffice to simply refer the reader to a paper by J. Irvine O. Masson (*Trans. Chem. Soc.*, **99**, 1132, 1911), in which such solubility problems are dealt with. For work on solubility in general the reader is referred to V. Rothmund's *Löslichkeit und Löslichkeitbeeinflussung* (Bredig's Series of Text-books).

CHAPTER VIII

Chemical equilibrium in heterogeneous systems modified by capillary and electro-capillary effects—Colloidal solutions.

IN this chapter it is proposed to consider the properties and conditions of equilibria which one finds in pseudo-solutions such as suspensions, emulsions, and colloidal solutions. [Phenomena connected with adsorption processes occurring either at the surfaces, *i.e.* interfaces between phases present in large continuous amount, *i.e.* "massive phases," or at the interfaces present in the above-mentioned colloidal solutions and emulsions, must be postponed for later thermodynamic treatment.]

Suspensions, Emulsions, Colloidal Solutions.—These all represent types of pseudo-solution. They differ from true solutions in that with suitable microscopic or ultramicroscopic apparatus it is possible to distinguish the individual particles of the "solute," which it is impossible to do in the case of solutes such as sodium chloride, etc. To the first class of substances which do not form true solution, *i.e.* substances in which the process of disaggregation does not reach the molecular limit when brought into contact with a liquid, Graham gave the name *colloids* to distinguish them from substances such as NaCl, urea, etc., to which he gave the name *crystalloids*. The first class of substances gives rise to heterogeneous solutions, the second class to homogeneous solutions. It must be remembered, however, that the transition between the two kinds of solution is gradual and not sharp. In fact, it is by no means easy to define exactly from this standpoint what we mean by a homogeneous solution unless we use a series of properties possessed by the one and not possessed (or only partially possessed) by the other type as arbitrary criteria. To show that

the transition between the two classes is gradual one may consider the property known as the Tyndall optical effect. When a beam of light is passed in a given direction through a medium containing fine particles in suspension the light is reflected from the particles, which are thereby made luminous and is partially polarised if observations are made at right angles to the direction of the beam. This phenomenon is exhibited by all colloidal solutions. It is not exhibited by true solutions, at least in ordinary dilutions. Cane sugar solutions, however, when very concentrated, exhibit the phenomenon, though a dilute solution of cane sugar is a typically homogeneous one. Suspensions, emulsions, and colloidal solutions differ as regards the size of particles—at least this is the only distinction so far made. It is doubtful, however, whether suspensions such as that of kaolin in water are really stable, *i.e.* whether they will remain in suspension for infinite time as colloidal solutions such as gelatine would certainly do, so far as our knowledge goes. Graham, as a matter of fact, regarded even colloidal solutions as really unstable, *i.e.* the colloid was in the act of precipitating itself, the process being an extremely slow one due to the smallness of the particles and the viscosity of the liquid medium. As regards our knowledge of these phenomena from the historical standpoint it is not necessary to say much, except to note that Graham, in 1862, was the first to study them scientifically and (as already mentioned) originated the name colloid. Graham's attention was drawn to this class of substances as a result of his experiments on diffusion of substances in solution (in water) through animal membranes. He found that while substances like common salt diffused readily, other substances like gelatine, albumen, silicic acid, did not pass through. He further found that solutions of these latter substances were very sensitive to the presence of acids and salts. He found, for example, that silicic acid or albumen could be precipitated from "solution" on adding a very small amount of HCl. Since the introduction of the electrolytic dissociation theory this effect has naturally been ascribed to the ions of the acid, base, or salt, and we shall study this more closely later. To the solution or pseudo-solution of silicic acid and other

colloids Graham gave the name *sol*, and to the substance after precipitation the name *gel*, since as a rule colloids assume the form of a gelatinous mass after being precipitated as above.

As examples of suspensions we may take kaolin or sulphur in water, or indeed any very finely divided solid. Emulsions consist generally of liquid particles distributed through a medium, *e.g.* milk (which consists of small particles of fat in suspension in water), rubber latex, and oil emulsions, which are obtained on vigorously shaking up a small quantity of an oil with water, or by dissolving the oil in a little alcohol and pouring the whole into water. To colloidal solutions belong substances such as starch, albumen, gelatine, silicic acid, many dyestuffs, certain hydroxides such as $(\text{Fe}(\text{OH})_3)_n$, certain sulphides such as $(\text{As}_2\text{S}_3)_n$, metals such as platinum in water. Colloidal solutions of metals are obtained most easily by Bredig's method of sparking electrodes of the metal under the surface of water, or by reduction of a salt to the metallic state, say, by formaldehyde.

Besides colloidal solutions in which water is the liquid medium, Svedberg (notably) has succeeded in preparing colloidal substances in organic solvents. Thus colloidal platinum can be prepared in the following solvents: amyl and ethyl acetates, the alcohols, acetone, ether, chloroform. Carbon and silicon form stable colloidal solutions in the higher alcohols. Pb, Sn, Zn form stable solutions in ethyl acetate and acetone. Cerium in isobutyl alcohol; Pt and Pd are also stable in isobutyl alcohol. For details the reader should consult Svedberg's book on the preparation of colloidal substances (*Herstellung Kolloider Lösungen*, Dresden, 1909).

As regards the characteristics of colloidal solutions, which are of course shared to different degrees by emulsions and suspensions, one may note the following: rate of diffusion, osmotic pressure, optical properties. These effects give us an indication of the size of the particles. Other characteristics are: the Brownian movement, the electric charge on the particles, and the phenomena of cataphoresis and endosmose, coagulation phenomena and protective effect, ferment action

of colloidal metals. We shall consider these points in some detail.

Diffusion and Osmotic Pressure.—As already mentioned in connection with Graham's work, colloids as a whole do not diffuse, or at most only slowly. Closely connected with this is the fact that their osmotic pressure is extremely small, for, of course, it is osmotic pressure which is the driving force as regards diffusion. The fact that the osmotic pressure is so small is shown by attempts made to measure it directly, and also by the lowering of vapour pressure of the solution and the lowering of the freezing point of water, say on adding substances such as starch or gelatine. Only an extremely small effect is observed, and as may be shown on thermodynamic grounds, small vapour pressure changes and freezing-point changes correspond to a small concentration or osmotic pressure, if indeed it is allowable to speak of concentration in the case of a solution which is heterogeneous. Measurements made have thus led to enormous values for the molecular weights of these bodies when in solution, *e.g.* :—

	M		M
Gelatine . .	5000	Albumen . .	14,700
Dextrin . .	1083	Gutta-percha ¹	40,000

It must be remembered that if the colloid is not pure—if, for example, it contains some electrolyte (as is frequently the case with dyestuffs prepared in the ordinary way by “salting out” by means of the electrolyte), even after prolonged dialysis—quite measurable osmotic pressure may be observed. This has been investigated especially by B. Moore, by Bayliss, and by Donnan. It is a well-established fact that many colloids of physiological origin can scarcely be freed from the electrolytes (NaCl) which accompany them in the tissues. So close is the adherence of these electrolytes to the colloid that it is customary to look upon the impure colloid as a loose chemical compound of colloid + electrolyte. The investigations of Moore and Roaf (*Biochem. Journal*) are among the most important in connection with this subject. For a discussion of

¹ Cf. Caspari, *Trans. Chem. Soc.*, **105**, 2139, 1914.

"forced membrane hydrolysis" and membrane equilibria, in which it is shown that an electrolyte such as NaCl does *not* distribute itself at equal concentrations on both sides of a parchment membrane when congo red is present on one side, one should consult a paper by Donnan and Harris (*Trans. Chem. Soc.*, **99**, 1554, 1911). Donnan's theory of such distribution effects is considered in Part II. (Vol. II.), Chapter X.

Optical Properties.—As regards optical properties of colloidal solutions that known as the Tyndall effect already mentioned is the most striking. It shows the existence of heterogeneity in a very direct manner. Attempts have also frequently been made to observe the particles and estimate their size by means of the microscope. This is not a difficult thing in the case of suspensions and emulsions. It fails, however, in the case of colloidal solutions such as those mentioned, owing to the small size of the particles. This has been overcome, however, in a very ingenious manner by Siedentopf and Zsigmondy by means of their ultramicroscope. In this instrument the field of view (of an ordinary good microscope) is kept dark and light enters transversely, *i.e.* horizontally. The tiny particles cause reflection of the light giving rise to images which are large enough to be visible and appear as bright, rapidly moving patches of light accompanied by diffraction rings in the microscope eyepiece. By this method, therefore, we are able to demonstrate the presence of extremely small particles; but, of course, we do not discern the actual particles themselves.

The Size of the Particles in Emulsions and Colloidal Solutions.—In the case of suspensions, the diameter of the particles as shown by an ordinary good microscope is mainly of the order 10^{-3} cm., though a considerable number of the particles are usually much smaller. Suspensions are as a rule very uneven.

In the case of emulsions, V. Henri has shown by the same means that rubber latex particles have a diameter between 10^{-4} and 10^{-5} cm. Lewis (*Zeitsch. Koll.*, **4**, 211, 1909) also showed that the diameter of hydrocarbon oil emulsion particles in water is approximately 4×10^{-5} cm. It was roughly

shown also that this appeared to be a *critical* size, *i.e.* an equilibrium size, in the following way: An emulsion was prepared by boiling a small drop of oil for many hours with a large quantity of water. The size of the particles was of the same order as in the emulsion prepared by vigorous shaking. A similar (and much more even) grained emulsion was obtained by dissolving the oil in a little alcohol and pouring the mixture into water. The diameter of the particles was again observed to be about 4×10^{-5} cm. In the previous methods this size of grain was reached by breaking down large masses; by the latter method the same value was reached by a process of limited coagulation from individuals of molecular size (oil molecules dissolved in alcohol form a "true" solution). It may also be mentioned that the milky emulsion formed in the receiver on distilling aniline in steam possesses grains of which the majority are of the order 10^{-5} cm. in diameter. Rapid coagulation to a "massive" oil layer takes place in this case, however, so that the emulsion is not a very stable one. This order of magnitude 10^{-5} is that predicted as an approximate result by Donnan on the basis of his thermodynamic theory (*Zeitsch. physik. Chem.*, 46, 197, 1903).

In the case of colloidal solutions the microscope, as already mentioned, is of no use. Thus Bredig showed that as a result of the *invisibility* of colloidal gold particles in water when viewed by a microscope, that the particles must have a diameter less than 0.14μ ($1 \mu = 10^{-4}$ cm.). Lobry de Bruyn considered that colloidal particles would not have a diameter *less* than $5-10 \mu\mu$ ($1 \mu\mu = 10^{-7}$ cm.), since smaller particles would not polarize light. A closer approximation may be obtained on the basis of the electromagnetic theory of light, according to which the wave-length λ , which suffers maximum absorption on passing through the colloidal solution, is connected with r the radius of the colloid particle by the relation—

$$r = \frac{\sqrt{3}}{4\pi n} \cdot \lambda$$

where n = refraction index of the medium (water). For colloidal gold solutions the maximum absorption occurred at

λ 490-520 $\mu\mu$. And hence r is 4.9 to 5.2×10^{-6} cm. (10^{-6} cm. = 10 $\mu\mu$). Similarly in the case of colloidal platinum, r comes out to be 4.8×10^{-6} cm., and for colloidal silver $(3.8 \text{ to } 4.8) \times 10^{-6}$ cm. Sir Joseph Thomson from other optical considerations (cf. *Recent Researches in Electricity and Magnetism*, p. 437) obtained a similar order of magnitude. Pockels and Zsigmondy and others, however, have come to the conclusion that the absorption band method is dependent on other factors, such as the shape of the particles and their chemical nature.

The most accurate method is by means of the ultra-microscope. The number of particles contained in a certain volume of solution can be counted, and the metal estimated by evaporating a certain much larger amount of solution and weighing the metal. Assuming the density of the particles to be approximately the same as that of the massive metal (in the ordinary form) the volume of each particle and hence the radius can be determined. In this way for colloidal gold particles (obtained by Bredig's sparking method) it has been found that $r = 2.8 \times 10^{-6}$ cm., for silver $r = 5.7.7 \times 10^{-6}$ cm.; for Pt, $r = 4.4 \times 10^{-6}$ cm.; for colloidal silver iodide $r = 6 \times 10^{-6}$ to 1×10^{-4} cm.; this latter is not stable, however, and assumes the gel form in a few days. As a rule particles greater than 10^{-6} coagulate after a short time.

The Brownian Movement.—The botanist Brown, in 1827, observed that fine suspensions and even very small gas bubbles suspended in a liquid medium are in a continuous state of vibration to and fro and up and down. This has been also observed for emulsion particles and still more for particles in colloidal solutions. The smaller the particles the greater the Brownian movement. It was first suggested by Ramsay and later by Gouy, and it has been conclusively proved in recent years by Perrin, that this is due to the collisions of the colloidal particles with the molecules of the medium (say water). And, indeed, he has employed this in a most ingenious manner to calculate the number of molecules in a gram molecule, as we have already seen (cf. Chap. I.).

The Electric Charge on the Particles.—That the particles in suspensions, emulsions, and colloidal solutions possess an electric charge is easily shown by placing the liquid in a U tube fitted with electrodes charged to a fairly high potential difference, when it will be found that the particles wander to one of the poles, *i.e.* the so-called cataphoresis phenomenon.¹ In this way it has been shown that the particles possess either a positive or negative charge; the majority being charged negatively when water is the medium. This is in agreement with the rule that when two substances are electrified by friction, the substance with the higher dielectric constant takes on a *positive* charge, the other being negatively charged. Water has a very high

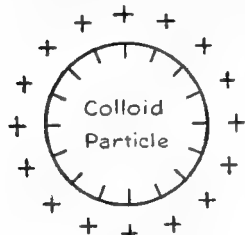


FIG. 33.—Illustrates the electric "double-layer." The positive charges are situated upon the molecules of the medium.

dielectric constant, and hence if we regard the origin of the charge on the particles as similar to frictional electricity, one would expect the water as a rule to be positive. As regards the charge carried by *suspensions*, Quincke showed in 1861 that the following substances in water travelled with the current, *i.e.* were *positively* charged (the water being negative): Quartz, kaolin, sulphur, lycopodium, air bubbles and bubbles of ethylene. [The results with air bubbles are surprising and some-

what doubtful.] No measurement of the charge has been made in any of these cases.

Lewis (*loc. cit.*) measured the velocity of movement of oil emulsion particles in water in an electric field, the potential difference between the electrodes being 230 volts. According to the Helmholtz-Lamb theory of the "double layer" of (+) and (−) electricity formed by friction (*cf.* Fig. 33), the following relation holds:—

$$V = \frac{4\pi}{K} \frac{\eta v}{X}$$

¹ Endosmose is the reverse of cataphoresis. Endosmose denotes the movement of a liquid along the walls of a fixed tube when a P.D. is put on the end.

where V is the P.D. between each particle and the water in contact with it (*cf.* Fig. 33).

K is the dielectric constant of water.

η is the viscosity of water.

v = velocity of the particle in centimetres per second under a P.D. gradient of X units per centimetre.

From this it was found that $V = 0.05$ volt for the emulsion oil particles suspended in water. Now we can write—

$$e = V \frac{r^2}{d} K$$

where e is the charge on the particle, d the thickness of the electrical double layer (which is supposed to be small compared to r , the radius of the particle). This formula will be referred to later. On substituting the data it is found that $e = 4 \times 10^{-4}$ *electrostatic units*. This should be compared with the values obtained for colloidal particles (see below).

We now pass on to consider *the electric charge carried by colloidal particles*. Investigation upon this subject was first undertaken by Linder and Picton (*Trans. Chem. Soc.*, 1892, p. 160). By the **U**-tube method already mentioned it has been shown that the following colloids (in water) are positively charged: hydroxides, *e.g.* $(\text{Fe}(\text{OH})_3)_n$, methyl violet, methylene blue, magdala red and other dyes. The following substances (in water) are negatively charged: colloidal metals, sulphur, sulphides, eosin, aniline blue, methylaniline green, etc. Hardy (*Journ. Physiol.*, 24, 288, 1899) showed that with albumen in a **U** tube in *alkali* a white coagulum collected at the anode, *i.e.* the colloid was negatively charged; whilst in *acid*, albumen is positively charged. In neutral solution it is practically stationary. This result obviously suggests that in the case of albumen, at any rate, the excess of H^+ ion or OH^+ is the determining factor. The sign of the charge on a given colloid depends to a large extent on the medium. Thus Billitzer has prepared (*Zeitsch. Koll.*, 1, 226, 1906) colloidal platinum in chloroform and found the metal positively charged, while in water it is negatively charged. On using a **U** tube with both solutions present, on applying the e.m.f., colloidal

platinum moved in opposite directions, meeting at the boundary of the water and chloroform interface.

One of the most satisfactory investigations carried out on the charge of colloids, and further on the conditions of its removal, is due to E. F. Burton (*Phil. Mag.*, [6], 11, 425; *ib.* 12, 472, 1906). The scope of his investigation may be briefly outlined.

Lamb (*Phil. Mag.*, p. 60, 1888) showed that the velocity of an isolated particle in an electric field is given by the expression—

$$v = X \frac{\rho}{\beta}$$

where v = velocity in centimetres per second.

X = potential gradient of the field in electrostatic units,
i.e. fall of potential per centimetre.

ρ = density of the charge on the particle, *i.e.* the charge
per square centimetre of surface.

β = is a small coefficient given by—

$$l = \frac{\eta}{\beta}$$

where l is called the “facility of slip” of the particle itself against the most immediate layer of molecules of the medium in which it is embedded. η is the viscosity of the medium.

Now $\rho = \frac{e}{4\pi r^2}$, where e is the charge on a particle, and r the radius of the particle (assumed to be spherical). Hence Lamb’s expression may be written—

$$v = \frac{Xe}{4\pi r^2} \cdot \frac{l}{\eta}$$

or
$$Xe = 4\pi r^2 \eta v \cdot \frac{1}{l} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We consider the small spherical particle as a condenser with “concentric plates” d cms. apart where d is small compared with r . That is, we assume the existence of a Helmholtz double layer of electricity of opposite sign surrounding the particle.

Since d is supposed small compared to r , the expression for the capacity C of the condenser arrangement takes the form

$$C = \frac{r^2 K}{d}$$

where K is the dielectric constant of the medium between the plates. Lippmann and others regard this as unity. Possibly a better approximation is to regard it as Burton does, as being that of the total medium itself, *i.e.* water say. Now if the P.D. between the particle and the medium, *i.e.* between the sides of the double layer, is V , we know that—

$$C = \frac{e}{V}$$

and therefore

$$e = V \cdot \frac{r^2}{d} \cdot K$$

Substituting this value of e in (1), we get—

$$V \left(\frac{l}{d} \right) = \frac{4\pi}{K} \frac{\eta v}{X}$$

Lamb (*l.c.*) has given reasons for believing that l and d are of the same order of magnitude (10^{-8} cm.), and Burton therefore regards $\frac{d}{l} = \text{unity}$ approximately. We have therefore

$$V = \frac{4\pi}{K} \frac{\eta v}{X}$$

which is the expression already employed on page 402. If the units on the right-hand side are electrostatic, in order to obtain V in volts we must multiply by the factor $(300)^2$, since 1 electrostatic P.D. unit = 300 volts, and X and v each involve this factor. Using the **U**-tube method Burton found the following values for the velocity v :—

WATER AS MEDIUM.

Colloidal substance.	Sign of charge carried by colloid.	Velocity in cms. per second under a gradient of 1 volt per cm.
Pt	(-)	20.3×10^{-5}
Au	(-)	21.6
Ag	(-)	23.6
Bi } (Probably <i>hydroxides</i> ,	(+)	11.0
Pb } though Burton does	(+)	12.0
Fe } not so regard them.)	(+)	19.0

The last three substances were the least stable, being precipitated from solution in a week.

ETHYL ALCOHOL AS MEDIUM.

Colloidal substance.	Sign of charge carried by colloid.	Velocity in cms. per second under a gradient of 1 volt per cm.
Pb } Hydroxides probably.	(+)	4.5×10^{-5}
Sn }	(+)	3.6
Zn }	(+)	2.8

Ag, Au, Pt, Bi, Fe, Cu could not be prepared in the form of stable solutions in ethyl alcohol.

METHYL ALCOHOL AS MEDIUM.

Colloidal substance.	Sign of charge carried by colloid.	Velocity in cms. per second under a gradient of 1 volt per cm.
Pb	(+)	22×10^{-5}
Bi	(+)	10.2

ETHYL MALONATE AS MEDIUM.

Colloidal substance.	Sign of charge carried by colloid.	Velocity in cms. per second under a gradient of 1 volt. per cm.
Pt	(-)	2.3×10^{-5}
Ag	(-)	1.7
Au	(-)	1.4

Bi, Pb, Zn, Fe could not be obtained as stable colloidal solutions.

Employing the equation given, Burton obtained the following values for the P.D. (V) between the particles and the respective media.

V IN VOLTS.

Nature of medium : Water.		Ethyl malonate.	C ₂ H ₅ OH.	CH ₃ OH.
Colloid.	K = 80 electrostatic units.	K = 10·7.	K = 25·8.	K = 33.
Pt	-0·031	-0·054	—	—
Au	-0·033	-0·033	—	—
Ag	-0·036	-0·040	—	—
Pb } hydroxides ?	+0·018	—	+0·023	+0·044
Bi }	+0·017	—	—	+0·022

(The *sign* (+ or -) denotes the sign of charge carried by the particles.)

Burton remarks on the similarity in the values for the P.D. in the different cases. The same order of magnitude was obtained by the writer for oil emulsion particles. It should be mentioned that according to Burton's measurements the size of the colloids was larger than that usually obtained by other workers. Burton found $v = 2$ to 5×10^{-5} cm. This does not come into the above expression for V, but does come into the calculation of e , the charge on the particle which is obtained by means of the expression

$$e = V \cdot \frac{r^2}{d} K$$

Burton did not calculate this, but it may be of some interest to work out a single case on his data. Take platinum colloid in water.

$$r = 2 \times 10^{-5} \text{ cm. (approx.)}$$

$$V = \frac{0\cdot031}{300} \text{ electrostatic units}$$

$$d = 5 \times 10^{-8} \text{ (Helmholtz's approximate value)}$$

$$K = 80 \text{ (electrostatic units)}$$

whence $e = 8 \times 10^{-5}$ electrostatic units.

For colloidal silver practically the same value is obtained. Of course these are only extremely rough values. Our knowledge of d may be in error to a very large extent. Its value may be ten times greater than that given. $\frac{l}{d}$ may not be unity at all, and this would throw out the values for V . We might make another attempt to measure e by applying Stokes' law¹ to the motion of the particle in the field (instead of employing Lamb's formula). Stokes' expression would be

$$e = \frac{6\pi\eta rv}{X}$$

Taking the case of silver colloid (using Burton's data for r , v , and X) one obtains $e = 8 \times 10^{-8}$ electrostatic units. It is doubtful whether the difference between this and the above value is real or is due to accumulation of errors. It should be pointed out, however, that the discrepancy is probably real, there being considerable doubt as regards the applicability of Stokes' expression, if we mean by the term e the total charge on the particle. Thus it is obvious that unless the layers of the Helmholtz "double layer" are able to slip at least to some degree past one another, the particle as a whole would not move at all in an electric field, for perfectly fixed electrical layers of equal and opposite sign would be an enclosed system with no apparent charge at all. In the above case, in applying the expression Xe as the electric force acting on the particle, we regard the particle as a point charge with an effective charge value e . Since, however, the slip is by no means complete, the value of e given by the Stokes' expression cannot be the total e on the particle which is given (approximately) on the basis of Lamb's formula, since the *facility of slip* is at least considered by Lamb, even though the allowance made for it may be approximate. It is probable, therefore, that the values of e given by Stokes' expression are really considerably less than the true value.

Burton has attempted to measure e by yet another method, depending on the amount of Al^{+++} ion required to precipitate

¹ Cf. W. C. McC. Lewis, *Zeitsch. Kolloide*, **4**, 209, 1909.

(or coagulate) a given amount of colloid. Before giving this method it will be necessary to consider the *coagulation phenomenon* itself.

Coagulation of Colloids.—It has been known for some time that on addition of a very small quantity of certain electrolytes to suspensions, emulsions, or colloids, the corresponding substances are thrown out of solution and form flocculent precipitates (gels), or in the case of oil emulsions, the oil collects as a layer on the surface.¹ It has been found that a certain minimum quantity of electrolyte is required to effect this. This quantity is far too small to make the process analogous to that of salting out, in which, as is well known, large quantities of the "salt" are required. Further, the operation seems to be of a very physical nature, depending on the sign of the charge carried by the suspended particle and practically independent of its chemical nature. *The important generalization is that ions carrying charge of sign opposite to that carried by the colloid are the most active precipitants, and at the same time the higher the valency of the ion (i.e. the greater the number of unit charges upon it) the greater its precipitating action.*

This is known as Hardy's Law. It might perhaps more legitimately be known as the Linder-Picton-Hardy Law.

This is clearly brought out by the following example dealing with the relative coagulating power of electrolytes required to precipitate a certain amount of colloidal $(As_2S_3)_n$ in water. This colloid is negatively charged, and hence positive ions of high valency exert the maximum coagulating effect. The coagulating power is simply the reciprocal of the molar concentration of the electrolyte required to precipitate all the colloid in a given time. Large coagulating power, therefore, means that a very small quantity of the given electrolyte is required. The coagulating power of KI in the table is taken as unity.

¹ One of the earliest investigations upon this subject is that of Ramsay (*Proc. Geol. Soc.*, 1876) upon the effect of salts on the settling of mud.

COAGULATION OF COLLOIDAL ARSENIC SULPHIDE.

Electrolyte.	Coagulating power of electrolyte.
KI	1.0
KCl	2.5
Na ₂ SO ₄	2.5
CaCl ₂	80
MgCl ₂	182
ZnSO ₄	60
Al ₂ Cl ₆	1518
Al ₂ (SO ₄) ₃	957

The great effect of A⁺⁺⁺ ion is here brought prominently into view. Similarly divalent ions such as Zn⁺⁺, Ca⁺⁺, Mg⁺⁺ are next in order of effect and monovalent ions are least effective. It is evident at the same time that the anion is having some kind of effect, *i.e.* KCl and KI are not identical in effect. The part played by the anion has never yet been cleared up. It is easily seen from the table, however, that the presence of an anion such as SO₄^{''} neutralises to some extent the effect of the cation, and one divalent anion possesses a greater neutralising effect on the cation than two monovalent ions, *e.g.* compare the coagulating power of Al₂Cl₆ and Al₂(SO₄)₃.

If the colloid is positively charged then of course the negative ions of high valency are the most effective precipitants, the cations in such a case exerting a hindering or neutralising influence. This is shown by the following data obtained by H. Freundlich (*Zeitsch. physik. Chem.*, **44**, 129 to 160, 1903) in the case of colloidal ferric hydroxide, *i.e.* (Fe(OH)₃)_n, which is positively charged in water. Instead of giving coagulating power the table gives the reciprocal of this, *i.e.* the minimal equivalent quantities of electrolytes required to precipitate a given quantity of the colloid in a given time—

COAGULATION OF $(\text{Fe}(\text{OH})_3)_n^+$

Electrolyte.	Minimal concentration of electrolyte required for precipitation.
NaCl	0.00925 mols per liter
KCl	0.00903 " "
$\text{BaCl}_2/2$	0.00964 " "
KNO_3	0.0119 " "
$\text{Ba}(\text{NO}_3)_2/2$	0.0140 " "
K_2SO_4	0.000204 " "
MgSO_4	0.000217 " "
H_2SO_4	0.0005 " "

It will be noted that K_2SO_4 has the greatest coagulating power, this being due to the strong divalent anion SO_4^{--} , which is only slightly retarded in its action by the two monovalent cations K' . When, for example, Ba'' or Mg'' is substituted for K' the coagulating effect of a given anion, say Cl' , is retarded, *cf.* BaCl_2 and KCl . Whetham has generalised the coagulating effects approximately in the following statement, which he deduced on the basis of the theory of probability (*Phil. Mag.*, 48, 474, 1889; *Zeitsch. physik. Chem.*, 33, 385, 1900), namely: *The coagulating power (i.e. the reciprocal of the minimal concentration) of a series of ions of the same sign is proportional to a constant raised to the power representing the valency of each ion (Whetham's Law).* If the coagulating powers of a mono-, di- and trivalent radicle are P_1 , P_2 , P_3 , then

$$P_1 : P_2 : P_3 = K : K^2 : K^3$$

This, however, does not allow quantitatively for the apparent effect of the oppositely charged ion, which of course is always present.

As regards the *kind* of union which takes place between the active ion and the colloid, practically nothing is known. It is generally regarded at the present time as an adsorption or surface solubility effect, to which we shall refer later. It has been shown—at least in some cases—that the ion is actually carried down with the coagulating colloid. Thus Linder and Picton (*Trans. Chem. Soc.*, 67, 63, 1895) showed

that when colloidal arsenic sulphide (negatively charged) was precipitated by BaCl_2 this salt was partly decomposed, a small quantity of $\text{Ba}(\text{OH})_2$ being found in the precipitate, which could not be washed out completely, even after prolonged trial, and simultaneously a little free HCl was found in the supernatant liquid. This close union, which in the above instance exists, between the barium ion (in the form of baryta) and the coagulated colloid, is found frequently in the case of other ions in physiological liquids containing organic colloids. Reference has already been made to an analogous phenomenon in dealing with the osmotic pressure of certain physiological colloids and dyestuffs.

Coagulation of a colloid is in certain cases a reversible phenomenon, though it is more frequently irreversible. Besides being brought about by the addition of electrolytes, it may also be caused by heating or cooling the colloidal solution as well as by electrolysis (more correctly speaking by cataphoresis), the particles being carried in virtue of their charges to one of the electrodes, where they become discharged and assume the gel form. (Reversible coagulation is only met with in certain cases, *e.g.* gelatine, when the coagulation has been brought about by temperature changes. It is never found when coagulation is brought about by addition of electrolytes.)

A very remarkable phenomenon in connection with coagulation is the *protective action* of other colloids also present in the solution. Thus colloidal platinum is rendered much less sensitive to coagulating agents by the addition of a little gelatine to the solution. The mechanism of the process is at present unknown.

It should be remembered that the colloidal state plays a greater rôle in ordinary chemical operations and reactions than is generally supposed. From the peculiar form in which substances (simple inorganic bodies) may be precipitated under certain conditions, it seems not unlikely that the colloidal state (sol and gel) represents at least a transition stage in such phenomena. Thus it is possible to precipitate barium sulphate (which is ordinarily a definitely crystalline substance) in a form not very different from a thin jelly, which passes

over more or less rapidly into the stable form. Further, in the electrolytic precipitation of metals, such as copper, the formation of a smooth deposit is assisted by the presence of a little gelatine in the bath—an effect which reminds one of the “protective action” mentioned above. This effect in the case of copper electrolysis has, however, been called recently in question. The coagulation phenomena observed in the case of colloids has also been observed in the case of suspensions and emulsions, though these have been less extensively investigated (*cf.* Bodländer, *Jahrbuch für Mineralogie*, 2, 147, 1893).

We are now in a position to return to the question of the electrical charge on a colloidal particle as determined by Burton (*l.c.*) from the amount of $\text{Al}_2(\text{SO}_4)_3$ just required to cause precipitation. Burton determined this by measuring the velocity of the colloid particle in an electric field when different amounts of electrolyte were present. The following data were obtained for colloidal silver in water :—

6.5 MILLIGRAMS SILVER PER 100 C.C. SOLUTION.

Grams of Al^{+++} ¹ per 100 c.c. solution.	Specific conductivity of the solution at 18°C.	Velocity of silver sol in cm. per second under 1 volt per cm. gradient.
0	31.0×10^{-6}	22.4×10^{-5} towards anode
14×10^{-6}	30.3×10^{-6}	7.2×10^{-5} „ „
38×10^{-6}	29.7×10^{-6}	5.9×10^{-5} „ cathode
77×10^{-6}	28.5×10^{-6}	13.8×10^{-5} „ „

The colloid, which by itself is negatively charged, becomes eventually positively charged on addition of $\text{Al}_2(\text{SO}_4)_3$, and at the region in which the Al^{+++} is 26×10^{-6} grams per 100 c.c. the velocity would be zero. This is called the *isoelectric point* (Hardy), and at this point the critical concentration of Al^{+++} is reached for coagulation. As a matter of fact, the colloid which travelled towards the cathode was very unstable, and precipitated itself after a short time. The velocity method is the most exact method for determining the coagulating point, *i.e.* the “critical” amount of electrolyte required.

¹ No allowance was made for hydrolysis of $\text{Al}_2(\text{SO}_4)_3$ giving rise to $\text{Al}(\text{OH})_3$, which is very slightly dissociated.

Burton in calculating the charge on the colloid assumed that the whole of the charged Al^{+++} ions took part, and gave up their complete charge to the colloid. He found that the volume of each colloidal particle was 2×10^{-14} c.c., and since the mass of colloid is 6.5 milligrams in 100 c.c., the number of particles present—assuming the ordinary density for the silver, which is a little doubtful—he calculated to be 3×10^{10} per 100 c.c. Now 1 gram-ion Al^{+++} carries $3 \times 96,550$ coulombs, that is, 26×10^{-6} grams Al^{+++} carry 0.289 coulomb, and since this was required for 3×10^{10} particles, the charge (of opposite sign) carried by each colloid particle is 9.6×10^{-12} coulombs or approximately 2.8×10^{-2} electrostatic units. The result given by Stokes' expression is 8×10^{-8} electrostatic units, and that by the more chemically sound expression of Lamb is 8×10^{-5} electrostatic units. There is no doubt, therefore, that Burton's result is much too large. If we assume Burton's value for ϵ and calculate the P.D. between the particle and the medium by means of the capacity expression, one finds $V = 33$ volts, which is of course quite impossible. For these reasons it has been suggested (Lewis, *Zeitsch. Koll., l.c.*) that only a small fraction of the critical concentration of the Al^{+++} ion is effective for coagulation. Lamb's expression yields the most trustworthy value—it is probably of the right order of magnitude. One other point requires to be mentioned, namely, that the charge on a colloid particle is several thousand times greater than that on a single electrolytic ion (*i.e.* if we assume the mass of one Al^{+++} is of the order 10^{-23} grams, then this carries a charge of 3×10^{-9} electrostatic units, since 27 grams carry $3 \times 96,550$ coulombs). It is, therefore, impossible to assume with Billiter that one ion is a centre of condensation for several colloid particles.

It is also of importance to remember that at the isoelectric point the Brownian movement ceases.

Rubber Latex (Emulsion).—From a technical standpoint, the most important emulsion which occurs as a natural product is rubber latex. Henri (Abstract, *Zeitsch. Koll.*, 1, 116, 1906) gives the following general characters of the latex. That obtained from Brazilian trees (Para rubber) reacts weakly

alkaline. Its density is 0.973. Its specific conductivity at 25° is 0.0033, which is the same as that of a 0.25 per cent. NaCl solution. The freezing point of the latex was -0.22°. This is the effect which would be produced by an N/9 solution of a non-electrolyte or an N/16 binary electrolyte. Salts (inorganic) are present in the natural latex, and the osmotic effects are due to these. An analysis of Venezuelan latex yielded the following results :—

Water	46.0	per cent.
Mineral matter	0.6	„
Mechanically held organic matter	1.7	„
Sugar and albumen	3.5	„
Resin	36.90	„
Gutta substance	11.30	„

On examination with the microscope a great number of particles were observed, approximately half of which possessed a radius 1 micromillimetre (10^{-4} cm.), the radius of the rest being 0.25 of one micromillimetre. Brownian movement was observed, especially among the smaller particles. The number of particles was determined by the ordinary physiological method of determining blood corpuscles. Henri found 50,000 particles per cubic mm.

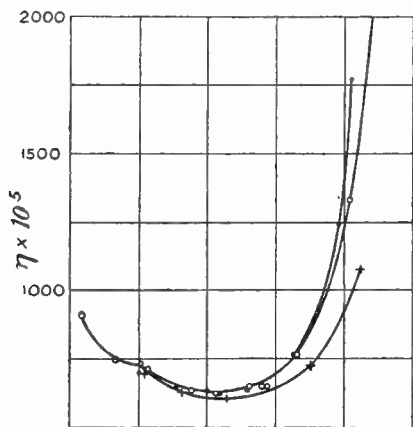
After prolonged dialysis Henri states that he obtained the latex almost free from salts. A U-tube cataphoresis experiment showed that the rubber particles were *negatively charged*. The effect of various precipitating agents was tried.

Alcohols had no effect on the dialysed substance (they caused precipitation of the undialysed substance). Monovalent salts were without effect. Divalent salts (Ba, Ca, Mg) caused precipitation (coagulation) if present at concentration above the normal. Salts of Mn, Fe, Ni, Co, Cu, Zn, Pb, Al, cause coagulation if present at the concentration N/20 approximately. Alkalies had scarcely any effect. Acids when about N/2 caused coagulation.

These effects are roughly what one would expect, remembering that the particles are negatively charged. The concentrations of the electrolytes are, however, very large

compared with those with which we have already dealt in the case of colloids. For recent work upon the colloid chemistry of rubber and caoutchouc, see Caspari, *Trans. Chem. Soc.*, 105, 2139, 1914.

The Viscosity of Colloidal Solutions containing Electrolytes.—In this connection reference may be made to a paper by F. D. Farrow (*Trans. Chem. Soc.*, 101, 347, 1912), who examined the viscosity of solutions of sodium palmitate (soap) in water in presence of varying amounts of electrolytes such as NaOH, NaCl, KCl. Sodium palmitate is partially hydro-



Concentration of electrolyte

FIG. 34.

lysed, and the products of hydrolysis have been shown to exist to a certain extent in the colloidal form. The material forming the colloidal particles is known as the "disperse phase," the medium in which the particles are suspended, as the "continuous phase." The viscosity curves obtained were similar in all cases, as is shown by the diagram (Fig. 34), which illustrates the effect of

varying concentration of electrolyte upon the viscosity of constant mass of sodium palmitate. The lowest curve refers to addition of KCl, the middle curve to NaOH and the uppermost to NaCl. On addition of electrolyte to a freshly prepared solution of sodium palmitate, a fall in the viscosity was observed, *i.e.* the viscosity tended in the direction of the value for pure water. On further addition of the electrolyte the viscosity increased. Woudstra (*Zeitsch. Kolloid.*, 8, 73, 1911) observed a similar behaviour in the case of colloidal ferric hydroxide. The sodium palmitate solution is heterogeneous, the disperse phase containing a

much higher ratio of alkali and fatty acid to water than is the case in the relatively much more dilute and continuous "water phase." According to Farrow, one may regard the disperse phase as bounded by a semi-permeable membrane across which equilibrium is set up by the various constituents. On adding an electrolyte it naturally dissolves in the continuous "water phase," and will exert osmotic pressure therein, the effect of which is to draw some water through the membrane of the disperse phase so that the concentration of water in the particles decreases, thereby causing the particles themselves to shrink in size, and hence exert a diminished effect upon the viscosity of the solution as a whole. This seems to be a reasonable explanation of the initial fall in viscosity. Another possible action of the electrolyte has to be taken into account, namely, the coagulating effect, such effect naturally becoming more pronounced the higher the concentration of the electrolyte. This causes the particles to coalesce, thereby forming larger aggregates, which produce an increase in the viscosity represented in Fig. 34, in the region of higher concentration of electrolyte. This view of the phenomena assumes that the larger the particles the greater the viscosity, and inversely. Woudstra (*loc. cit.*) has shown experimentally that this assumption is a correct one in the case of the inorganic colloids examined by him. For further information upon the viscosity of colloidal solutions, the reader should consult the report of the discussion upon the subject published in the *Transactions of the Faraday Society*, 1913.

Theories of the Coagulation of Colloids.—In this connection a number of "theories" have been put forward, many of which are little more than a restatement of some experimental fact which itself requires explanation. First of all we have Hardy's electrical theory. In this it is assumed that an electrical charge, *i.e.* a P.D. between the colloid and the medium (say H_2O), is necessary to the stability of the colloid. When by the addition of ions of opposite sign the colloid particle loses its P.D. with respect to the solvent, the isoelectric point is reached and coagulation occurs. Hardy makes further assumptions about the electrical work required for

the vibration of the colloid particles, which, however, are of a very hypothetical nature. Bredig has gone a step further in regarding the phenomenon as an electrocapillary one. Lippmann has shown that there is a connection between the surface tension at a phase surface and the charge on the surface. By altering the potential and plotting the corresponding values of surface tension, he obtained a curve which passed through a maximum value (for the surface tension) when the external *e.m.f.* was applied in a certain direction, *i.e.* when it was used to neutralise the natural P.D. possessed by the surface. When a surface is uncharged its surface tension is therefore greater than when it is charged. Hence at the isoelectric point, the surface tension on the colloid particle is a maximum. This may mean that the surface potential energy is a maximum, and according to Bredig coagulation occurs in order to reduce this, as will certainly happen since the surface area of the coagulated mass is much less than that of the free colloid particles. As regards the mechanism of the action of the precipitating electrolyte, Bredig applies Nernst's idea of the distribution of two ions between the phases, *viz.* the colloid particles and the medium. If these solubility coefficients are not the same for both ions then preferential solubility will occur, and hence set up a P.D. at the surface. If, therefore, the cation is more soluble in the colloid than the anion, it will tend to give a positive charge to the colloid, and if the latter is negative to start with the electrolyte may discharge it. Freundlich's theory is somewhat analogous to Bredig's with the important distinction, however, that instead of regarding the ions as *soluble* in the colloid, the effect is restricted to the surface. The P.D. is then set up by the preferential adsorption, or surface condensation of one ion to a greater extent than the other. This, which undoubtedly is the most satisfactory explanation of the mechanism of the process of discharging the colloid, will be appreciated better when we have studied the phenomena known as adsorption in Part II. (Vol. II.), Chap. X. All these theories, however, deal with the process whereby the electrical charge on the colloid is neutralised ; they do not offer more than a qualitative

explanation of why coagulation occurs when the isoelectric point is actually reached.

Theory of the Stability of Colloidal Solutions.—We are now discussing the question of the conditions which determine the stability of a colloidal solution when *no* electrolyte is present. In this we are undoubtedly dealing with an electrocapillary phenomenon.¹ No satisfactory theory on this basis has, however, yet been put forward. The only attempt at such is that of Donnan, which, however, is restricted to capillary effects alone, the probable part played by the electrical charge not being considered. At the same time the importance of Donnan's conclusions warrants a short recapitulation here (*cf.* F. G. Donnan, *Phil. Mag.*, 1, 647, 1901).

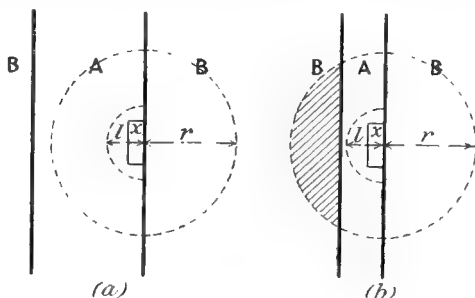


FIG. 35.

The basis of Donnan's theory is the assumption that the range of molecular attraction (*i.e.* the distance throughout which the attraction due to a single molecule is still perceptible) varies from substance to substance. This is an extremely likely assumption. Suppose now we have a strip of substance A (*i.e.* the colloid substance) immersed in a liquid medium B (Fig. 35 (a) and (b)).

Consider a small particle or volume element X at the interface of A and B. Then the total attractive effect of B upon A may be represented by a large semicircle, its radius r being the range of the molecular attraction of the molecules

¹ For a preliminary attempt to deal with this problem, see a paper by the writer (*Zeitschr. Kolloide*, 5, 91, 1909).

composing B. Also the smaller semicircle, radius l , represents the attractive force pulling X into A. Suppose $r > l$. Now, if the strip of substance A be shaved down until it is very thin (until its thickness is as in Fig. 35 (*b*), in which the thickness is still greater than l , but less than r), then there will now be an effective portion of B pulling X in the opposite sense to its original effect, the extent of this oppositely directed effect being given by the shaded segment. The total effect of B upon X tending to draw it in the original direction is less than before, and we can evidently imagine that a critical value for the thickness of the strip may be reached at which the pull on X in opposite directions due to l and the "weakened" r effect would just balance one another. When this is reached there will be no further tendency of A to split into a finer state of division. For thicknesses greater than the critical, the body A has a tendency to *increase* its common surface with B, *i.e.* it possesses an effectively *negative* surface tension. For thicknesses less than the critical (l now greater than the *effective* r) there will be a positive surface tension, and hence smaller aggregates of A will tend to grow to the critical size. "If a colloid be defined as a substance which forms these pseudo-solutions termed colloidal, it follows from the above that this description is not sufficient unless the other medium—the pseudo-solvent—be specified. This point is well illustrated by the result obtained by Krafft with the soaps; these substances give true solutions with alcohol, and colloidal solutions with water." This possibility was first mentioned by W. B. Hardy.

For further information upon colloid chemistry in general, the reader should consult Müller's *Allgemeine Chemie der Kolloide* (Bredig's Series of Text-books of Applied Physical Chemistry), H. Freundlich's *Kapillarchemie*, Zsigmondy's *The Ultramicroscope*, Wolfgang Ostwald's *Grundriss der Kolloidchemie*, and the various volumes of the *Zeitschrift für Chemie und Industrie der Kolloide* ("Kolloidzeitschrift").

CHAPTER IX

Systems not in Equilibrium—Treatment from the Kinetic Standpoint—
Homogeneous Systems: Diffusion of Solutes in a Solution—Reaction
 Velocity—Types of Reactions—Catalysis.

*Diffusion of Solutes in Solution.*¹—The motion of a dissolved substance from one part of a solution to another, represents the simplest type of “chemical” kinetics in a homogeneous system. It was first quantitatively examined by Nernst (*Zeitsch. physik. Chem.*, **2**, 613, 1888), who employed as a fundamental assumption the validity of Fick’s Law (*Pogg. Ann.*, **94**, 59, 1855), viz. the quantity of salt which diffuses through a given area is proportional to the difference between the concentrations at two areas infinitely near to each other. That is, if we take two points in a solution at an infinitesimal distance apart dx , the difference in concentration at these two points will be $d\epsilon$, and hence the concentration gradient in the direction x will be $\frac{\partial \epsilon}{\partial x}$. Fick’s Law states that, for the case when the diffusion is in one direction only, as occurs when it is allowed to take place in a cylinder, the amount of solute dS which will cross a given cross-section area a , in a time dt , is expressed by—

$$dS = -Da \frac{\partial \epsilon}{\partial x} dt \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or the rate of change by—

$$\frac{dS}{dt} = -Da \frac{\partial \epsilon}{\partial x} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The minus sign here denotes that the solute diffuses in the direction of decreasing concentration. *D* is the so-called

¹ See R. Haskell (*Physical Review*, **27**, 145, 1908), from whose paper this section is mainly taken.

diffusion constant or specific diffusion rate; it is equal to the amount of solute which would diffuse across unit area under a concentration gradient of unity in unit time if the rate were constant during that time. In this work the time is expressed in days, the concentration in equivalents per liter, and the distance in centimetres. Now consider an infinitesimal volume in a cylinder bounded by planes at the distance x and $x + dx$. The amount of solute which will accumulate in this volume in time dt will be the difference in the amount which will cross the planes at x and at $x + dx$. That is—

$$\left[dS - \left(dS + \frac{\partial(dS)}{\partial x} dx \right) \right] \text{ or } - \frac{\partial(dS)}{\partial x} dx$$

The increase in concentration of the solute in time dt in this volume, then, is the total accumulation divided by the volume, or—

$$- \frac{\frac{\partial(dS)}{\partial x} dx}{adx}$$

As this may also be expressed by the quantity $\frac{\partial c}{\partial t} \cdot dt$ we get—

$$\frac{\partial c}{\partial t} dt = - \frac{1}{a} \frac{\partial(dS)}{\partial x}$$

Substituting for dS its value $-D \cdot a \cdot \frac{\partial c}{\partial x} \cdot dt$ given by Fick's Law, carrying out the differentiation, and eliminating dt , we obtain as our reduced equation for the case, in which the cross-section is uniform—

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \cdot \cdot \cdot \cdot \cdot \cdot (3)$$

This equation is analogous to that of Fourier for the flow of heat, and has different solutions according to the conditions imposed by the methods of carrying out the diffusion. If in a tube so long as to be practically infinite, so far as the time of an ordinary experiment is concerned, the concentration is held constant at one end and is zero at the other, and if at the start the concentration is zero throughout the tube, we may obtain by solving the differential equation under the assumption that D is constant the following

expression for the concentration c at any point x after any time t —

$$c = c_0 \left(1 - \frac{2}{\sqrt{\pi}} \int_0^u e^{-u^2} \right) \quad . \quad . \quad . \quad . \quad (4)$$

where c_0 is the concentration at the lower end, and—

$$u = \frac{x}{2\sqrt{Dt}}$$

Knowing the value c for any point we can inversely calculate D , the diffusion constant. If D is not constant for all values of c , as is the case if the assumption of the different rates of diffusion of the dissociated and undissociated substances is true, another formula must be developed which will take this fact into consideration.

Nernst considers the case of electrolytes which he assumes to be completely dissociated. In this way we have to deal with only one diffusion coefficient, since the electrical force practically prevents the ions separating, and the slow one is hastened, the faster one delayed, so that both travel together. Assuming the solute to be totally dissociated, Nernst derived theoretically an expression for D in terms of the ionic velocities as computed from transference and conductivity data for the case of a salt splitting into two univalent ions. For the more general case in which the salt is completely dissociated into any number of ions, an expression may be similarly derived,¹ as follows:—

Let us take an electrolyte whose molar weight yields on complete dissociation n_c mols of cations of valence v_c and n_a mols of anions of valence v_a . The product of the number of mols of each ion by its valence is necessarily the same for both the positive and negative ions (for electric neutrality); or $n_c v_c = n_a v_a$. If C is the concentration of salt in mols per liter, the number of ions having the same electrical sign is $n_c C$ for the cation and $n_a C$ for the anion (*i.e.* $n_c C = n_a C =$ gram ions or mols per liter); and correspondingly the concentration gradients for the cation and anion are $\frac{n_c dC}{dx}$ and

¹ For this derivation Haskell is indebted to Professor A. A. Noyes. Since it is cast in an extremely neat form I quote it practically word for word.

$\frac{n_a dC}{dx}$, respectively. As the osmotic pressure of the ions is expressed by $P = nCRT$, the force acting across unit area through the distance dx in the positive direction of x is the difference between the force P at x and $P + dP$ at $x + dx$, or is—

$$-n_a RT \frac{dC}{dx} dx \quad \text{and} \quad -n_c RT \frac{dC}{dx} dx$$

for the anions and cations respectively. This is the force that acts upon the ions in the volume dx (the sectional area being unity), that is upon $n_a C dx$ and $n_c C dx$ mols of anions and cations so that the force acting upon one mol will be—

$$\frac{-n_a RT \frac{dC}{dx} dx}{n_a C dx} = \frac{-n_c RT \frac{dC}{dx} dx}{n_c C dx} = -\frac{RT}{C} \cdot \frac{dC}{dx} \quad (5)$$

it being therefore identical for both the anion and cation. Now, since the friction against the solvent is different for the different ions, one ion would tend to get ahead of the other. This, however, would generate an electrostatic field between the positive and negative ions, which field in turn would accelerate the slower ion and retard the more rapidly moving one. Let us consider the electric potential generated to be E , then the electric force acting upon one mol of cation or anion is—

$$-v_c F \frac{dE}{dx} \quad \text{or} \quad +v_a F \frac{dE}{dx}$$

respectively, where F is one faraday of electricity. The total force acting upon one gram ion or mol therefore is—

$$-RT \frac{1}{C} \cdot \frac{dC}{dx} - v_c F \frac{dE}{dx} \quad \text{for the cations} \quad . \quad . \quad (6)$$

$$-RT \frac{1}{C} \cdot \frac{dC}{dx} + v_a F \frac{dE}{dx} \quad \text{for the anions} \quad . \quad . \quad (7)$$

Let u_c and u_a be the velocities of each ion when the force acting upon one mol or gram ion is unity, and let dN_c and dN_a be

the number of gram ions of each ion passing a cross-section a in time dt , then under the above force—

$$dN_c = u_c a n_c C \left(-RT \frac{1}{C} \cdot \frac{dC}{dx} - v_c F \frac{dE}{dx} \right) dt^1 \quad (8)$$

$$dN_a = u_a a n_a C \left(-RT \frac{1}{C} \cdot \frac{dC}{dx} + v_a F \frac{dE}{dx} \right) dt. \quad (9)$$

But $\frac{dN_c}{n_c}$ = the fraction of one gram ion of the cations passing the section in time dt . $\frac{dN_a}{n_a}$ has the same significance for the anion. Therefore—

$$\frac{dN_c}{n_c} = \frac{dN_a}{n_a} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

since equivalent quantities of the two ions must pass through any section in the same time, it follows that—

$$u_c \left(RT \frac{1}{C} \cdot \frac{dC}{dx} + v_c F \frac{dE}{dx} \right) = u_a \left(RT \frac{1}{C} \cdot \frac{dC}{dx} - v_a F \frac{dE}{dx} \right) \quad (11)$$

$$\text{or} \quad F \frac{dE}{dx} = - \left(\frac{u_c - u_a}{u_c v_c + u_a v_a} \right) \frac{RT}{C} \cdot \frac{dC}{dx} \quad (12)$$

If this value be substituted in equation (8) or (9), and further substitution be made in equation (10) above, we have—

$$\frac{dN_a}{n_a} = \frac{dN_c}{n_c} = \left\{ \begin{array}{c} dN \\ \text{or} \\ dS \end{array} \right\} = - a RT \frac{dC}{dx} \left\{ \frac{u_a u_c (v_a + v_c)}{u_c v_c + u_a v_a} \right\} dt \quad (13)$$

where dN or dS is the number of molar weights passing cross-section in time dt . By comparison of (13) with (1) we see that—

$$D = RT \left\{ \frac{u_a u_c (v_a + v_c)}{u_c v_c + u_a v_a} \right\}$$

If instead of molar weights we use equivalent weights, since

¹ For u_c = velocity of ion = number of cms. traversed by the ion per second. $u_c a$ = volume of solution swept out, *i.e.* passing over a plane in unit time. If concentration is $n_c C$, *i.e.* the number in unit volume, then $n_c C \times u_c a$ = number of gram ions passing through the plane per unit time when under unit force. With above force the number dN_c in time dt is $n_c C u_c a \times \text{total force} \times dt$.

one molar weight equals $n_c v_c$ or $n_a v_a$ equivalents, and $U_c = u_c v^c$ and $U_a = u_a v_a$ represent the velocities when unit force acts on one equivalent weight of ions,¹ we obtain by substitution and reduction—

$$dS = - aRT \frac{dc}{dx} \cdot \frac{U_a U_c}{U_a + U_c} \left(\frac{1}{v_c} + \frac{1}{v_a} \right) dt \quad (14)$$

where dS is the number of equivalents crossing in time dt , and where $\frac{dc}{dx}$ represents the concentration gradient in equivalents.

By a comparison of this formula with the expression of Fick's Law (equation (1)), we see that we can express D in terms of quantities derived from electrical measurements, or—

$$D = RT \frac{U_a U_c}{U_a + U_c} \left(\frac{1}{v_c} + \frac{1}{v_a} \right) \quad . \quad . \quad . \quad (15)$$

provided, of course, we assume that the solute is totally dissociated, and hence all diffusion is done by the ions only. This condition is approached only in very dilute solutions, and hence D is the limiting value at infinite dilution. At other concentrations the value of D as found from Fick's formula will be greater or less according as the undissociated substance diffuses faster or slower than the ions. *As a general rule, the diffusion constant has been shown to become larger as the dilution is increased, and hence, we believe that the ions move more rapidly than the undissociated portion.*

The typical experimental arrangement for investigating the above expression consists of a long vertical cylinder, with solid salt at the bottom, the diffusion takes place upwards. The retarding influence of gravity Haskell shows to be negligible, and the above arrangement has the advantage of keeping the denser portions of the solution at the bottom, so that no stirring or mixing effects enter. The tube is of such a length that the experiment can be completed—the time is measured in days—before any salt reaches the top. The concentration at different

¹ If unit force acts on one equivalent, then v_c times this force acts on one *mol* or gram ion. If u_c be velocity of the cation when unit force acts on one equivalent of the ion, then $v_c u_c$ is the velocity when the above force acts on one gram ion, for velocity \propto force always.

levels can be determined, by measuring the electrical conductivity, by means of small electrodes situated in pairs at various heights in the tube. This was the general arrangement employed, for example, by Haskell.

ÖHOLM'S DIFFUSION CONSTANT DATA AT 18° C. (*Zeitsch. phys. Chem.*, **50**, 309, 1905). [These values were obtained graphically from actual determinations carried out at different temperatures in the neighbourhood of 18° C.]

Normality.	NaCl.	KCl.	LiCl.	KI.	HCl.	CH ₃ ·COOH.	NaOH.	KOH.
5·5	1·065	—	—	1·549	—	—	—	—
4·2	—	—	0·956	—	—	—	—	—
3·6	—	1·338	—	—	—	—	—	—
2·8	1·064	—	—	1·434	—	—	—	—
2·00	—	1·320	0·928	—	—	—	1·259	1·892
1·00	1·070	1·330	0·920	1·366	2·217	0·833	1·290	1·855
0·50	1·077	1·345	0·919	1·372	2·188	0·856	1·310	1·841
0·20	1·098	1·367	0·929	1·380	2·202	0·871	1·342	1·843
0·10	1·117	1·389	0·951	1·391	2·229	0·884	1·364	1·854
0·05	1·139	1·409	0·971	1·412	2·251	0·895	1·386	1·872
0·02	1·152	1·431	0·980	1·428	2·285	0·910	1·404	1·889
0·01	1·170	1·460	1·000	1·460	2·324	0·930	1·432	1·903

The values of *D* at concentration 0·01 *N* may be taken as referring to practically complete dissociation of the substance in all cases except that of the weak acid CH₃·COOH. The following are some of the values of *D* calculated and observed :—

Substance.	<i>D</i> ₁₈ observed (Öholm).	<i>D</i> ₁₈ calculated (Öholm).
NaCl	1·170	1·173
KCl	1·460	1·460
LiCl	1·000	0·994
KI	1·460	1·467
HCl	2·324	2·431
CH ₃ ·COOH . . .	0·930	1·368
NaOH	1·432	1·558
KOH	1·903	2·109

The agreement is good, and the relation between mobility

of ions under an electric field, and diffusion under no external field as given by the expression for D is therefore justified.

Öholm's Determination of the Temperature Coefficient of Diffusion.—If D_{t_0} and D_{t_1} be the diffusion coefficients for a given substance at temperatures t_0 and t_1 respectively, then the temperature coefficient α is given by the expression—

$$\alpha(t_1 - t_0) = \frac{D_{t_1} - D_{t_0}}{D_{t_0}}$$

or
$$\frac{D_{t_1}}{D_{t_0}} = 1 + \alpha(t_1 - t_0)$$

In this expression α is the fractional increase in D due to 1° rise in temperature. α is usually given as the fractional increase in D for 10° rise in temperature, and the following values for α have this significance. The reason for adopting this convention will be clear when we come to study the problem of temperature coefficients of purely chemical reactions (page 462 *seq.*) and the problem of heterogeneous catalysis (page 497 *seq.*). The following values are calculated from Öholm's mean values (*L.c.*, p. 331):—

Substance.	α .	$\frac{D_{t_0 + 10}}{D_{t_0}}$
NaCl	0.25	1.25
KCl	0.235	1.235
LiCl	0.27	1.27
KI	0.235	1.235
HCl	0.19	1.19
CH ₃ ·COOH .	0.28	1.28
NaOH	0.23	1.23
KOH	0.21	1.21

Öholm points out that the smaller the diffusion constant D is, the greater is the value of the temperature coefficient of D . The same relation holds good for the electrolytic conductivity of these substances and its temperature coefficient. In fact, Öholm concluded that the temperature coefficient of diffusion was equal to the sum of the temperature coefficient of the osmotic

pressure (identical in dilute solutions with the temperature coefficient of gaseous expansion) + the temperature coefficient of the electrical conductivity.

Haskell has studied more closely the case of a dissociated solute diffusing in two parts, the dissociated and the undissociated. During an infinitesimal time the parts may be considered as moving independently, each having its own diffusion coefficient.¹ Hence we can say that the total amount crossing the area is equal to the sum of the two parts, that is—

$$dS = dS_1 + dS_2$$

Haskell works out a differential expression for this which, however, he cannot integrate. He therefore has to employ approximate methods of solution by introducing empirical relationships connecting x , t , and c in his experiments with thallium sulphate and barium nitrate. These salts were investigated in decinormal solutions, and are to a large extent undissociated. The results obtained were as follows :—

Salt.	D_1 unionised salt.	D_2 ions.
Ti_2SO_4 . . .	0·77	1·56
	0·80	1·50
$\text{Ba}(\text{NO}_3)_2$. .	0·69	1·40
	Mean 0·785	Mean 1·53

It is thus seen that the rate of diffusion of the undissociated substance is one-half that of the ions. The friction encountered by the molecules is therefore double that encountered by the ions.

REACTION VELOCITY IN HOMOGENEOUS SYSTEMS.

We may have two cases :—

- (1) Isolated reactions, *i.e.* a single reaction unaccompanied by any side reaction, and
- (2) Simultaneous reactions.

¹ Nernst. *Zeitsch. phys. Chem.*, **2**, 634, 1888.

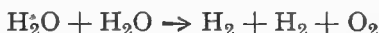
1. *Isolated Reactions.*

By way of introduction it may be necessary to define fairly rigidly what is meant by the velocity of a chemical reaction. The first thing to be noted about practically all chemical reactions is that they do not progress at a constant rate. They start off rapidly under certain given conditions, and as time goes on the reaction becomes slower. A determination of the quantity of substance transformed divided by the time taken would therefore not give us a reliable numerical value characteristic of the reaction, for the value would evidently vary with the *stage* at which we examined the reaction. What we must attempt to do, therefore, is to connect the infinite number of different instantaneous velocities—each of which we denote by the symbol $\frac{dx}{dt}$, where x is the amount of substance transformed—together by some expression or law, in the form of a differential equation, which after integration will give us some numerical value or values—a constant or constants, in fact—characteristic of the processes under investigation. The law referred to is the Law of Mass Action, and in its most general form, as applied to chemical kinetics, may be defined as follows:—

The rate at which a body takes part in a chemical reaction is proportional to its active mass. When we are dealing with a system in which the term “concentration of a component” has a definite meaning, and this type of system is the usual one in homogeneous chemical kinetics—in such a case the most general form of the Law of Mass Action may be expressed thus: The rate at which a substance takes part in a reaction is proportional to its concentration raised to a certain power—this power being numerically identical with the number of molecules of the substance required to satisfy the chemical equation which represents the reaction. Thus let us take the case of water decomposing into hydrogen and oxygen. The stoichiometric equation is—



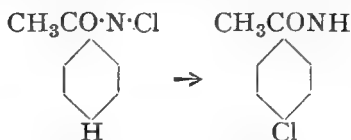
and the law of mass action states, therefore, that the rate at which the water molecules participate is proportional to $C_{H_2O}^2$, the rate at which H_2 molecules participate (in tending to reform water) is proportional to $C_{H_2}^2$, and the rate at which the oxygen molecules tend to participate is simply proportional to C_{O_2} . The simplest conceivable measure of the reactivity of a substance is, of course, to put it proportional to the concentration. A reaction such as that above can then be rewritten—



and we might regard each constituent represented by each molecular symbol as different—though the process is rather artificial—when we see at once that the rate at which the constituents of the left-hand side are reacting is $\propto C_{H_2O} \times C_{H_2O}$, which gives us again the form $C_{H_2O}^2$. Similarly in the case of the H_2 molecules we arrive at the expression $C_{H_2}^2$ as the measure of the reactivity of H_2 in this reaction.¹

Chemical reactions are conveniently divided into classes according to their stoichiometric equations, and consist of one molecule, two, three, etc., giving rise to any number of resultants. The names employed are monomolecular, bimolecular, termolecular, etc. We shall consider these in order.

Monomolecular Reactions.—An instance occurs in the transformation of dissolved acetochloranilide into *p*-chloracetanilide—



According to the law of mass action the rate at which the acetochloranilide is participating, *i.e.* disappearing, at any moment is proportional to its concentration (for the power to which the concentration term is to be raised is unity). This may be written in the form of a differential equation—

$$\frac{dx}{dt} = k(a - x)$$

¹ Or, on the theory of probability, the chance that two molecules A and B come into contact is proportional to the product of their concentrations.

where x is the amount of the acetochloranilide transformed at any time, a is the original quantity started with, $(a - x)$ being the amount left at any time t , and k is a constant. We want to evaluate k , and to do so it is evidently necessary to integrate the equation. This is done as follows:—

The expression
$$\frac{dx}{dt} = \frac{-d(a - x)}{dt}$$

and therefore
$$\frac{-d(a - x)}{dt} = k(a - x) \text{ or } \frac{-d(a - x)}{a - x} = k dt$$

or
$$-\log(a - x) = kt + \text{constant of integration.}$$

When $t = 0$ (the starting time) $x = 0$ (no reaction has occurred), and hence applying the above integration expression to this point, it is evident that the constant of integration $= -\log a$. Hence the integrated expression may be written—

$$-\log(a - x) + \log a = kt$$

or
$$\frac{1}{t} \log \frac{a}{a - x} = k$$

This expression can be used to evaluate k . Thus the following data were obtained (Blanksma, *Rec. Trav. Pays-Bas*, **21**, 366, 1902; **22**, 290, 1903) for the reaction referred to, the extent x of the reaction being determined at different time intervals by removing an aliquot portion of the solution, adding KI and titrating the liberated free iodine with thiosulphate; *p*-chloracetanilide does not react with KI while acetochloranilide does. Blanksma's results are:—

t in hours.	$a - x$, i.e. C.C.S. of thiosulphate.	k .
0	49.3	—
1	35.6	0.139
2	25.75	0.140
3	18.5	0.140
4	13.8	0.138
6	7.3	0.138
8	4.8	0.139

The constancy of the values in the last column is conclusive,

evidence for the correctness of our considerations and the applicability of the monomolecular equation.

A similar type of reaction velocity, perhaps more correctly a heterogeneous reaction velocity, is exemplified by many radioactive transformations, notably the decay of thorium X with time (when isolated from thoria itself) investigated by Rutherford and Soddy (*Trans. Chem. Soc.*, 81, 837, 1898). If we omit the initial part of the process for reasons which will be clear when we have studied so-called "consecutive simultaneous reactions" (page 447), the following data are given for the rate of decay of isolated Th X (deposited on a platinum wire, say). The units are of course arbitrary.

Time in days from start.	Activity of Th X.
2	100
3	88
4	72
6	53
9	29.5
10	25.2
13	15.2
15	11.1

In this case a is = 100. Employing the expression

$k = \frac{1}{t} \log \frac{a}{a-x}$ we obtain the following results:—

t intervals.	$a - x.$	$\frac{1}{t} 2.3 \log_{10} \frac{a}{a-x} = k.$
$0 = \left\{ \begin{array}{l} \text{arbitrary} \\ \text{initial} \\ \text{point} \end{array} \right\}$	100	—
1	88	(0.128)
2	72	0.168
4	53	0.159
7	29.5	0.174
8	25.2	0.172
11	15.2	0.171
13	11.1	0.169
		Mean = 0.169

Another instance is afforded, in the case of the rate of decay of radium emanation (niton).

Decay of Radium Emanation (Rutherford and Soddy, *Phil. Mag.*, [6] 5, 445, 1903).—The emanation—which is itself a gas—mixed with air was obtained from a solution of radium chloride and kept in a closed bottle. It was stored over mercury in an ordinary gasholder. From time to time equal quantities were measured off by a gas pipette and delivered into the testing vessel, which consisted of a brass cylinder having a central insulated electrode. A sufficient voltage to obtain the saturation current was applied between the central rod and the cylindrical shell, the central rod being at the same time connected to an electrometer. The ionisation current immediately after the introduction of the emanation furnished the measure of the activity of the latter. The measurements were repeated over a period of 33 days before the effect became too small to be accurately determined. The following results were obtained:—

Time in hours.	Relative activity of the emanation.
0	100
20·8	85·7
187·6	24·0
354·9	6·9
521·9	1·5
786·9	0·19

From the above values it may be observed that the activity falls off in a geometrical progression with the time; the time taken for the activity to fall to half its original value being 3·71 days, this result being obtained by substituting in the simple exponential or monomolecular expression—

$$I = I_0 e^{-\lambda t} \text{ or } \frac{1}{t} \log \frac{I_0}{I} = \lambda$$

where I_0 is the initial activity (measured by the magnitude of the saturation current), and I the activity after time t .

A recent determination of the rate of decay of radium

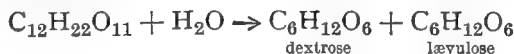
emanation is that given by Rümelin (*Phil. Mag.*, 14, 550, 1907), who found that the period of half decay was 3·75 days; Ramsay has, however, found 3·18.

Rate of Formation of Radium Emanation (Rutherford and Soddy, *loc. cit.*).—Radium chloride was dissolved in water and a current of air aspirated through the solution. After a few hours the radio-activity of the salt obtained from the solution was found to have been reduced to a minimum, and continued aspiration over three weeks did not affect it. It was inferred, therefore, that all the emanation had been removed, and now it was possible, after evaporating the solution to dryness, to determine the rate of formation of the emanation by measuring the activity of the radium salt at different intervals of time. The following results were obtained :—

Time in days.	Activity.	% Activity recovered.
0	25·0 {the non-separable activity}	0
0·70	33·7	11·7
1·77	42·7	23·7
4·75	68·5	58·0
7·83	83·5	78·0
16·0	96·0	95·0
21·0	100·0	100·0

The two sets of values corresponding to the decay of the emanation and its rate of formation were found to be exactly complementary.

Another important monomolecular reaction which takes place in aqueous solution, especially in the presence of acid, is the inversion of cane sugar into dextrose and lævulose according to the equation—



The reaction is catalysed, *i.e.* hastened, by the presence of H^+ , and its velocity may indeed be used as a measure of the concentration of the latter. It might appear at first sight that

this is a bimolecular reaction, as is certainly the case according to the stoichiometric equation, for in all, two molecules appear on the left-hand side. The rate of the reaction may therefore be written $\propto C_{\text{sugar}} \times C_{\text{H}_2\text{O}}$. But since the $C_{\text{H}_2\text{O}}$ is constant at all stages of the reaction (since we are dealing with dilute aqueous solution), the term $C_{\text{H}_2\text{O}}$ may be moved into the factor of proportionality and we conclude that the rate at which the reaction proceeds is simply proportional to the concentration of cane sugar—and as only one molecule of this is involved in the stoichiometric equation, the power to which the concentration term is raised is unity. Hence for the inversion of cane sugar—which can be followed experimentally in a polarimeter, since the products of the reaction, *i.e.* the resultants dextrose and lævulose, rotate the beam of polarised light in a different direction to cane sugar—we find the expression

$$\frac{1}{t} \log \frac{a}{a-x} = k$$

gives actually constant values for k , and hence the reaction is monomolecular. The following results may be given by way of illustration :—

INVERSION OF CANE SUGAR. $a = 10.023$.

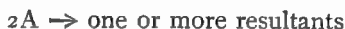
t mins.	x .	k .
0	0	—
30	1.001	0.00152
60	1.946	0.00156
90	2.770	0.00156
130	3.726	0.00155
180	4.676	0.00151

One must be on one's guard, therefore, in studying a new reaction, in attempting to find out from the nature of the velocity constant, how many molecules are taking part. Often the velocity constant does actually tell us how many molecules take part, but it is also seen from the above illustration that a substance may be actually taking part in the mechanism of

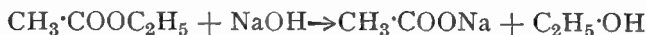
the reaction, but if its concentration is not thereby affected, *e.g.* the water, its presence will not be made clear, in the type of velocity constant obtained.

Now let us consider bimolecular reactions.

Bimolecular Reactions.—These may be represented by—



A typical instance is the saponification of an ester by an alkali, *e.g.* ethyl acetate and caustic soda¹ in aqueous solution reacting according to the equation—



During the reaction the concentration of both the alkali and ester decreases, and since the equation involves only one molecule of each, we see by the law of mass action that the rate at which the resultants are being formed is—

$$\frac{dx}{dt} = kC_{\text{CH}_3\cdot\text{COOC}_2\text{H}_5} \times C_{\text{NaOH}}$$

The reaction is a bimolecular one.

Suppose we start with equivalent amounts of ester and alkali, say a gram-moles in a certain volume which remains constant throughout the reaction, and let x be the amount of each transformed at time t , then the velocity expression is—

$$\frac{dx}{dt} = k(a - x)(a - x) = k(a - x)^2$$

To obtain k we must integrate. As before—

$$\frac{dx}{dt} = \frac{-d(a - x)}{dt}$$

and hence $\frac{-d(a - x)}{dt} = k(a - x)^2$ or $\frac{-d(a - x)}{(a - x)^2} = kdt$

and therefore $\frac{1}{a - x} = kt + \text{integration constant.}$

¹ See footnote to page 326.

When $t=0$ $x=0$, and therefore the integration constant $=\frac{1}{a}$, and hence the integrated expression may be written—

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

or
$$\frac{1}{a-x} - \frac{1}{a} = kt \text{ or } \frac{1}{t} \frac{x}{a(a-x)} = k$$

The following data show the applicability of the above equation to the saponification¹ of ethyl acetate by NaOH, both these substances being present initially at the same equivalent concentration $a = \frac{N}{50}$, temp. 26° C.

Time t in minutes.	$(a-x)$ = amount of NaOH not yet transformed, as given by the c.c. of $\frac{N}{8}$ oxalic acid required for the titration of 100 c.c. removed from the solution at time t . (The value assigned to a must be expressed in the same units.)	k .
5	10.24	5.625
15	6.13	5.37
25	4.32	5.405
35	3.41	5.27
55	2.31	5.385
120	1.10	5.645
		mean 5.45

The constancy of k is fairly evident throughout.

It is not necessary, however, to start with equivalent amounts of the two substances in a bimolecular reaction. Suppose the initial quantity of ethyl acetate $= a$ and the initial quantity of alkali $= b$ in the given reaction; further, if x is the amount transformed at time t , *i.e.* number of moles of each transformed (for the disappearance of one mole of ester necessarily entails the disappearance of one mole of alkali, as is evident from the stoichiometric equation), the velocity expression is—

$$\frac{dx}{dt} = k(a-x)(b-x)$$

¹ Warder, *Ber.*, **14**, 1361, 1881.

and on integration this becomes—

$$\frac{1}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} = k$$

If one of the reactants—say that to which a refers—is present in very large excess, as is the case in the action of water on sugar during its inversion, we can neglect its change in concentration during the reaction, *i.e.* we can neglect x and b likewise compared to a . The above equation then becomes—

$$\frac{1}{ta} \log \frac{ba}{a(b-x)} \quad \text{or} \quad \frac{1}{ta} \log \frac{b}{b-x} = k$$

and since a is necessarily constant—being simply the initial arbitrarily chosen concentration of water—we can rewrite the equation in the form—

$$\frac{1}{t} \log \frac{b}{b-x} = k_1$$

which is evidently identical with the monomolecular velocity expression previously obtained for such a case. An interesting instance of a “bimolecular reaction” is to be found in the rate of recombination of the ions (oppositely electrified particles), in a gas which has been subjected to some ionising agency, such as radium rays or ultraviolet light, and then removed from the action of the ionising agency. What happens is that one positive particle unites with one negative particle to give once more two neutral gas molecules. The work of Rutherford, Townsend and others has shown that the following expression holds good :—

$$\frac{1}{N} - \frac{1}{N_0} = kt$$

where N is the number of ions in the gas after a time t , N_0 the number of ions originally present in the gas, and k is a constant known as the coefficient of recombination of the gas. If we write $N_0 = a$ and $N = (a - x)$ the above expression simplifies down to the one for a bimolecular reaction in which equivalent quantities of the reactants are present.

Termolecular Reactions.—The reaction of this type may be

represented by any one of the following stoichiometric equations:—



The differential equation corresponding to the first case in which all the substances are present at different initial concentrations a, b, c , will be—

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

In the case of the second type of stoichiometric equation, or in the first type in which $a = c$, we have the velocity equation—

$$\frac{dx}{dt} = k(a-x)^2(b-x)$$

In the case of the third type of stoichiometric equation, or in the other two types, provided the initial concentrations are the same, that is, $a = b = c$, we find that the velocity equation is—

$$\frac{dx}{dt} = k(a-x)^3$$

Let us integrate this simplest form—

$$\frac{dx}{dt} = - \frac{d(a-x)}{dt}$$

$$\therefore \frac{-d(a-x)}{(a-x)^3} = kdt$$

or $+ \frac{1}{2}(a-x)^{-2} = kt + \text{integration constant}$

When $t = 0$ $x = 0$, and the integration constant $= \frac{1}{2a^2}$, and hence the integrated form may be written—

$$\frac{1}{t} \cdot \frac{1}{2} \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\} = k$$

This equation may be illustrated by the polymerisation of cyanic acid into cyamelide (van 't Hoff, *Études*, 90, 1884) and by the interaction of ferrous chloride, potassium chlorate and

hydrochloric acid investigated by Noyes and Wason (*Zeit. physik. Chem.*, **22**, 210, 1897).

Quadrimeric Reactions.—There are only a few of such reactions known. The most general type of reaction velocity equation for four substances at different initial concentrations, a, b, c, d is—

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)(d-x).$$

The simplest case is that in which the initial concentrations are identical— $a = b = c = d$.

Thus
$$\frac{dx}{dt} = k(a-x)^4$$

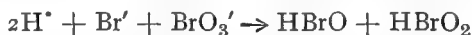
and on integration—

$$\frac{1}{t} \cdot \frac{1}{3} \left\{ \frac{1}{(a-x)^3} - \frac{1}{a^3} \right\} = k$$

By way of illustration, we may take the case of the reaction between HBr and HBrO₃, which was found to give a constant belonging to the quadrimeric order (Judson and Walker, *Trans. Chem. Soc.*, **73**, 410, 1898). In aqueous solution at 25° the following data are given :—

t in minutes.		k .
2	Initially the volume	0'000000117
4	= 100 c.c.	0'000000115
6	containing	0'000000111
8	5 c.c. HBr solution	0'000000112
10	5 c.c. HBrO ₃ „	0'000000109
15		0'000000110
20		0'000000111
30		0'000000115
60		0'000000115

The conclusion arrived at was that the reaction was an ionic one—



(the substances on the right-hand side being both practically undissociated). This was borne out by the fact that when the

reaction was carried out in fairly strong sulphuric acid, *i.e.* in large excess of H^+ , the reaction became apparently bimolecular, *i.e.* the $[H]$ term is constant, and therefore the reaction may be written—



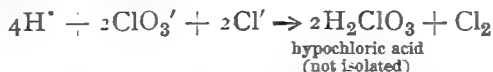
Compare this case with that of the inversion of cane sugar in which a bimolecular reaction gives a monomolecular constant.

Quinquemolecular Reactions.—The only example of this type is that furnished by the reaction between potassium ferricyanide and potassium iodide (Donnan and Le Rossignol, *Trans. Chem. Soc.*, 83, 703, 1903). We shall consider this later when we come to the question of determining the *order* of a reaction. [It should be mentioned, however, that Just (*Zeitsch. physik. Chem.*, 63, 513, 1908) has reinvestigated the problem, introducing *e.m.f.* measurements as well as velocity measurements, and has come to the conclusion that this reaction is trimolecular, *i.e.* monomolecular with respect to potassium ferricyanide and bimolecular with respect to potassium iodide.]

Reaction of the Eighth Order.—R. Luther and F. H. McDougall (*Zeitsch. physik. Chem.*, 62, 199, 1908) have investigated the action of HCl on $HClO_3$ in aqueous solution. When the chlorion (Cl') content is not too great the stoichiometric equation is—

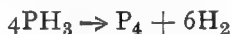


The velocity measurements showed that the chief reaction occurring was—



i.e. an eighth-power reaction on the left-hand side. As a matter of fact, an equilibrium is finally set up, owing to the opposing reactions, examples of which will be studied later. (The *order* of the reaction was determined by van 't Hoff's method of varying the initial concentration and measuring the initial velocity.)

Comparison of Stoichiometric Equations and Velocity Equations.—It must be noted that frequently the stoichiometric equation does not necessarily correspond to the velocity equation. In general the velocity equation is of a simpler type. This is shown by the fact that there are numerous mono- and bimolecular reactions known, that is to say, using the corresponding velocity constant as the *criterion*, we find very many instances of reactions which yield good constant values for these simpler types. The instances of trimolecular reactions are more scarce, the quadrimolecular still more rare, and so on. On the other hand, many stoichiometric equations involve a large number of molecules. Take as an example the decomposition of phosphine, PH_3 . Stoichiometrically we represent this reaction by the equation—



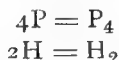
P_4 being the constitution of the phosphorus molecule. Instead of this reaction giving a quadrimolecular constant, it gives a monomolecular one, as is shown in the table below (König, *Zeitsch. physik. Chem.*, **12**, 155, 1892).

<i>t</i> in hours.	Pressure of gaseous mixture.	<i>k</i> calculated as monomolecular constant.	<i>k</i> calculated as quadrimolecular constant.
0	715.21 mm.	—	—
7.83	730.13 "	0.00236	0.0173
24.17	759.45 "	0.00237	0.0201
41.25	786.61 "	0.00235	0.0229
63.17	819.96 "	0.00238	0.0288
89.67	855.50 "	0.00241	0.0385

The fact that a monomolecular constant is obtained suggests that the reaction goes in two stages, namely—



followed by—



these being extremely rapid compared to the first.

For it is evident that it is the slowest reaction in a series which will determine the resultant velocity of the whole.

[For an alternative and not unlikely explanation of the above phosphine case, cf. Mellor, *Statics and Dynamics*, p. 57. Whichever explanation is correct does not, however, affect the distinction which in many cases must be drawn between stoichiometric molecular numbers and velocity molecular numbers.]

The Characteristic Distinctions between Reactions of Different Orders.—The simplest velocity equations characteristic of reactions of different orders are, as we have already seen—

For monomolecular reactions $\frac{1}{t} \log \frac{a}{a-x} = k$

For bimolecular reactions $\left\{ \begin{array}{l} \text{Equivalent} \\ \text{quantities} \end{array} \right\} \frac{1}{t} \cdot \frac{x}{a(a-x)} = k$

For termolecular reactions $\left\{ \begin{array}{l} \text{being} \\ \text{present} \\ \text{initially} \end{array} \right\} \frac{1}{t} \cdot \frac{1}{2} \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\} = k$

and so on.

These expressions are sufficiently different from one another, as a rule, though not always, that if one of them represents the reaction under investigation, the others cannot, *i.e.* the others will give inconstant values for k .

Now let us consider the question of the time taken to decompose one-half of the original substance, and see how this time varies in the different orders. We are considering the instant at

which $x = \frac{a}{2}$. On substituting this value in the monomole-

cular type we obtain the expression $\frac{1}{t} \log 2 = k$. $\log 2$ is of course a constant itself, and hence we find that the value of t is a constant, being expressible simply in terms of $\log 2$ and k . This means that t —where t is the time required for half decomposition of the substance—is independent of the value of a . That is, if we start with a 1 normal solution of a substance or with a $\frac{N}{10}$ solution of the same substance, the time taken for half of the substance to be decomposed in each case is the same.

Now take a bimolecular reaction (in which as a simplification we assume equivalent initial amounts of both substances).

When $x = \frac{a}{2}$ the bimolecular expression becomes—

$$\frac{1}{t} \cdot \frac{\frac{a}{2}}{a \cdot \frac{a}{2}} = k \quad \text{or} \quad \frac{1}{t} \cdot \frac{1}{a} = k$$

That is, the time required for half decomposition is *not* independent of a , the initial concentration of the reacting substances. As one sees, t is inversely proportional to a . Thus, if we start with $\frac{N}{1}$ and $\frac{N}{10}$ solutions, respectively, of the reacting mixture, the time taken for the reaction to proceed to the one-half stage is different in the two cases. In fact, the time of half decomposition in the case of the normal initial concentration will be one-tenth of the time taken for half decomposition in the case of the $\frac{N}{10}$ solution. Again, in the case of termolecular reactions, we see on substituting $x = \frac{a}{2}$ that the time t is inversely as the square of the initial concentration, and that in general for an n molecular reaction the time ($t_{\frac{1}{2}}$) required for half decomposition is inversely proportional to the $(n - 1)$ power of the initial concentration (each component being assumed present initially at equivalent concentrations). Hence in general we may write—

$$t_{\frac{1}{2} \text{ decomposition}} \propto \frac{1}{a^{n-1}}$$

These considerations lead us naturally to take up the question: To what order does a given reaction belong? for we have seen that the stoichiometric equation itself is not always identical with the velocity equation which determines the reaction.

METHODS OF FINDING THE NUMBER OF MOLECULES PARTICIPATING IN A REACTION.

A. The most direct method is to measure the rate of the reaction by suitable means at given intervals of time, and simply work out the values of k , which are given by the different expressions for mono-, bi-, termolecular reactions, and the order which gives the most constant value for k is the order assigned to the reaction. This method is unsatisfactory when complicating side reactions occur—to which we shall come shortly.

B. We may introduce the ideas with which we were dealing, when it was shown that the time of half decomposition was $\propto \frac{1}{a^{n-1}}$. Suppose we take a reaction and make measurements using two different initial concentrations a_1 and a_2 . Then if t_1 and t_2 are the times of half decomposition in each case—

$$\frac{t_1}{t_2} = \frac{a_2^{n-1}}{a_1^{n-1}}$$

From which n can be obtained.

This method, however, may be made more useful by being generalised as follows. Consider the intervals of time t_1 and t_2 (for the same reaction) required for the transformation of the same fractional part (not necessarily one half) of the original substance, and carry out the same process of reasoning as before. Thus suppose we denote the fractional amount transformed by ϕ . That is to say, if in two experiments a_1 and a_2 denote the initial concentrations of the reacting bodies, then let t_1 and t_2 denote the respective intervals of time in which x has reached the values ϕa_1 and ϕa_2 in each instance. It may be easily seen that if the reaction is monomolecular, and the term ϕa be introduced instead of x , we find t independent of a . If the reaction is bimolecular, we find that t is inversely as a , and so on. In fact, we find the same expression as before, viz.—

$$t \propto \frac{1}{a^{n-1}}.$$

Hence, applying this expression to the two cases mentioned, we obtain—

$$\frac{t_1}{t_2} = \frac{a_2^{n-1}}{a_1^{n-1}}$$

or
$$n = 1 + \frac{\log \frac{t_1}{t_2}}{\log \frac{a_2}{a_1}}$$

C. Van 't Hoff's differential method is less accurate than the foregoing, and need not be discussed at length: *cf.* Mellor's *Statics and Dynamics*, p. 59.

D. *Ostwald's Isolation Method.*—This method really involves the artificial simplification of a reaction, *i.e.* the lowering of its order by the use in turn of a large excess of all components except one. The mode of reaction of each is thus determined separately.

Having now discussed the various types of reaction velocities in relation to isolated reactions, *i.e.* those which are not complicated by additional reactions, it is necessary to take up the question of several reactions occurring at the same time. These are known as *simultaneous reactions*.

2. Simultaneous Reactions.

When several reactions occur at the same time in a given system we are dealing with simultaneous reactions. These may be divided into three classes.

- (1) Side reactions.
- (2) Consecutive reactions.
- (3) Opposing reactions.

A side reaction is one in which a reactant gives rise to more than one independent resultant, *e.g.*



in which B and C may not have any chemical affinity for one another.

Consecutive reactions may be represented by the scheme



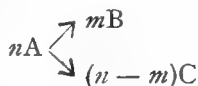
Opposing reactions are those in which the reaction does not go to an end, but an equilibrium is reached of the type dealt with at length in considering homogeneous equilibrium, *e.g.*—



We shall consider these three classes of simultaneous reactions in turn.

A. SIDE REACTIONS.

In the case represented by—



$+\frac{dx}{dt}$ will be the rate of formation of both B and C observed together.

$-\frac{dx}{dt}$ denotes the rate of disappearance of A.

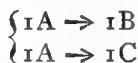
$+\frac{dy}{dt}$ „ „ appearance of B.

$+\frac{dz}{dt}$ „ „ „ „ C.

Then we have at any moment the relation—

$$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt}$$

Suppose we consider monomolecular reactions, *i.e.*—



then $\frac{dy}{dt} = k_1(a - x)$, where a is the original amount of A, and x is the amount of A transformed at the moment in question.

Similarly $\frac{dz}{dt} = k_2(a - x)$

$$\therefore \frac{dx}{dt} = k_1(a - x) + k_2(a - x) = (k_1 + k_2)(a - x)$$

which gives on integration—

$$\frac{1}{t} \log \frac{a}{a-x} = k_1 + k_2 = K \text{ say} \quad . \quad . \quad (1)$$

Now to evaluate k_1 and k_2 separately we must know some other connection between them. This connection appears if we remember that the rate of formation of B or C at any moment is the product of the respective velocity coefficients k_1 or k_2 into the amount of the original substance $(a-x)$ present. But $(a-x)$ is the same for each side reaction. So that the ratio of rate of formation of B to that of C, or what is the same thing, the ratio of the amount of B formed at any moment to the amount of C at the same moment, is simply the ratio of the velocity coefficients. That is—

$$\frac{\text{Amount of B at any stage}}{\text{Amount of C at the same stage}} = \frac{k_1(a-x)}{k_2(a-x)} = \frac{k_1}{k_2} = L$$

We can take as the most convenient stage the end of the reaction, and estimate the relative amounts of B and C formed, the ratio giving us $\frac{k_1}{k_2} = L$. With this information we can now obtain k_1 and k_2 separately with the aid of equation (1). For evidently—

$$k_1 = \frac{KL}{L+1} \quad k_2 = \frac{K}{L+1}$$

and K and L are directly measurable quantities.

Holleman (*Zeitsch. physik. Chem.*, **31**, 79, 1899) showed that the nitration of benzoic acid with excess of nitric acid, resulted in the formation of *o*-, *m*- and *p*-nitro-benzoic acids as mono-molecular side reactions.

Reactions of higher orders may be treated in a similar manner.

Wegscheider's Test for Side Reactions (distinguishing them from Consecutive or Opposing Reactions).—We have really introduced Wegscheider's principle in the evaluation of the ratio $\frac{k_1}{k_2} = L$. It is: *The ratio between the amount of the substances formed in two side reactions is independent of the time.*

For monomolecular side reactions—



$$\text{Rate of formation of B} = \frac{dB}{dt} = k_1[A]$$

$$\text{,, ,, ,, C} = \frac{dC}{dt} = k_2[A]$$

$$\therefore \frac{\text{Rate of formation of B}}{\text{Rate of formation of C}} \text{ or } \frac{\text{quantity of B present at any time}}{\text{quantity of C present at any time}} \\ = \frac{k_1[A]}{k_2[A]} = \text{constant L independent of time.}$$

Similarly for polymolecular side reactions, *each of which involves the same number of A molecules*, we have—

$$\frac{dB}{dt} = k_1[A]^n$$

$$\frac{dC}{dt} = k_2[A]^n$$

$$\text{and } \frac{\text{Ratio of B formed}}{\text{Ratio of C formed}} = \frac{k_1[A]^n}{k_2[A]^n} = \begin{cases} \text{constant independent} \\ \text{of time} \end{cases}$$

Note, however, that for side reactions which do *not* involve the same number of molecules of A, *i.e.* $\begin{cases} n\text{A} \rightarrow \text{B} \\ m\text{A} \rightarrow \text{C} \end{cases}$

$$\text{then } \frac{dB}{dt} = k_1[A]^n \quad \frac{dC}{dt} = k_2[A]^m$$

and hence—

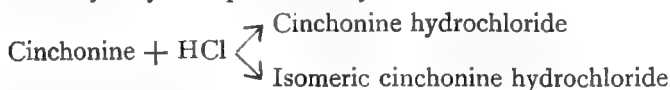
$$\frac{\text{Rate of formation of B}}{\text{Rate of formation of C}} = \frac{\text{quantity of B present at any moment}}{\text{quantity of C present at any moment}} \\ = \frac{k_1}{k_2} [A]^{n-m}$$

which is dependent on time. Hence Wegscheider's test has this limitation.

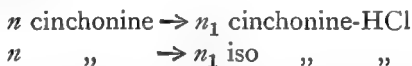
The utility of Wegscheider's method may be illustrated by the following example. Skraup showed that when a strong acid—such as hydrochloric acid—acts on cinchonine it forms cinchonine hydrochloride, and at the same time an isomeric

form of cinchonine hydrochloride (the isomerism of course exists in the cinchonine residue). Skraup considered that the reactions are consecutive, the ordinary hydrochloride being first formed, and the isomeric form being produced from this in turn. Wegscheider pointed out, however, that the quantities of ordinary hydrochloride and its isomer were in constant ratio to one another, independent of the time chosen for measurement. Hence the reactions must be side reactions and not consecutive.

So they may be represented by—



or more accurately—



where n appears actually to be unity in this case.

Note that if it had required a *different* number of cinchonine molecules to form the normal hydrochloride and iso-hydrochloride respectively, the reactions might still have been side reactions, but Wegscheider's test would have failed. A further instance of the applicability of Wegscheider's method is found in the monomolecular decomposition of camphor carboxylic acid $\text{C}_{10}\text{H}_{15}\text{O}.\text{COOH} \rightarrow \text{C}_{10}\text{H}_{16}\text{O} + \text{CO}_2$, which, in alcoholic solution undergoes esterification at the same time with practically the same speed. The results obtained by Bredig and Balcom (*Ber.*, 41, 740, 1908) support Wegscheider's principle very completely.

B. CONSECUTIVE (SIMULTANEOUS) REACTIONS.

An important principle to be remembered in connection with consecutive reactions is that, in a series of reactions occurring consecutively, the slowest one determines the order of the reaction. In fact, if one reaction of the series is very slow compared to the others, we may even fail to detect the presence of these others, at least by velocity constant measurements. We have already found such an instance in the dissociation of

phosphine PH_3 , which instead of involving four molecules only involves one, the main (slow) reaction being $\text{PH}_3 \rightarrow \text{P} + 3\text{H}$ followed by the much faster formation of the respective molecules P_4 and H_2 from the atoms. There are a number of reactions, however, which show by certain abnormalities in the velocity constant (when one attempts to fit results to some of the simple velocity equations) that consecutive changes are in operation. The general treatment of such cases—which unfortunately cannot go far owing to mathematical difficulties—may be illustrated by the simplest case, namely, the two consecutive monomolecular reactions $\text{A} \rightarrow \text{B} \rightarrow \text{C}$.

Starting with a mols of A, suppose that after a time t , there are now x mols of A remaining, and y mols of B and z mols of C are now in existence. The first relation we have is—

$$x + y + z = a \quad \dots \quad (1)$$

Also the rate of disappearance of A, namely $-\frac{dx}{dt}$, is given as usual by the relation—

$$-\frac{dx}{dt} = k_1 x \quad \dots \quad (2)$$

where k_1 is the velocity constant of transformation of A into B. The rate of formation of C is—

$$+\frac{dz}{dt} = k_2 y \quad \dots \quad (3)$$

where y is the concentration of B at the time t , C being formed from B with the velocity coefficient k_2 . Now the rate at which B accumulates in the system is evidently the difference between the rate of its formation from A (namely $-\frac{dx}{dt}$, where $-\frac{dx}{dt} = k_1 x$) and its own rate of transformation into C, namely

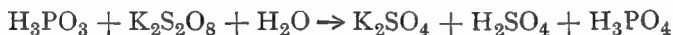
$\frac{dz}{dt} = k_2 y$. Hence—

$$\begin{aligned} \frac{dy}{dt} &= -\frac{dx}{dt} - \left(+\frac{dz}{dt}\right) = -\frac{dx}{dt} - \frac{dz}{dt} \quad \dots \quad (4) \\ &= k_1 x - k_2 y \end{aligned}$$

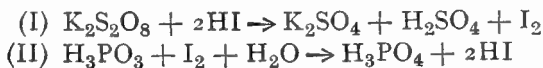
From the four relations given it is found on integration that $x + y$, i.e. the amount of A left in the system + the actual amount of B present at time t , or what is the same thing, the expression $a - z$, is given by the relation—

$$a - z = a \left(\frac{k_2}{k_1 - k_2} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right) \quad (5)$$

where we have written x in the form $ae^{-k_1 t}$. For certain mathematical reasons (for which see Mellor, *ibid.*, p. 98) the above expression cannot be rigidly tested in actual cases unless we know k_1 and k_2 separately. It may be illustrated—though the actual mathematical calculations were not actually carried out by using the above formula, owing to the rather complicated nature of the reaction—by the reaction between potassium persulphate and phosphorous acid in the presence of hydriodic acid. Without the HI the reaction, which is then an exceedingly slow one, is represented by—



In the presence of HI, however, the solution is seen to go brown, evidently due to the formation of iodine. The total reaction is then believed to be composed of two parts in succession—



The sum of the two is evidently identical with the previous one as far as final products are concerned. Now equation (I) was investigated by itself by Price (*Zeitsch. physik. Chem.*, **27**, 476, 1898), the velocity constant being 0.0065. This reaction corresponds to the disappearance of A in the preceding theoretical discussion and $k_1 = 0.0065$. Reaction (II) has also been investigated, this corresponding to the formation of the body C and $k_2 = 0.157$. The total reaction has been investigated by Federlin (*Zeitsch. physik. Chem.*, **41**, 565, 1902), and the following table contains some of his results :—

<i>t</i> hours.	Iodine.		Persulphate.	
	Observed.	Calculated.	Observed.	Calculated.
0.5	4.55	3.44	8.08	9.13
1.0	5.39	4.58	4.89	6.72
1.5	5.05	4.84	3.13	4.98
2.0	4.18	4.64	2.17	3.64
2.5	3.38	4.22	1.49	2.68
3.0	2.59	3.68	1.01	1.94

Note that the iodine goes through a maximum. The shape of the curves shown on the diagram (Fig. 36) is very characteristic of consecutive reactions.

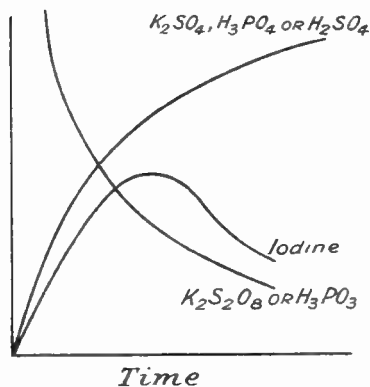


FIG. 36.

Another example of consecutive reactions is afforded by the saponification of dicarboxylic esters, such as ethyl succinate by alkali. If the reaction is treated as a bimolecular one, we find that the "constant" will fall to less than half its initial value. The mechanism, therefore, seems to be, that there are two reactions in succession.

(1) The formation of ethyl sodium succinate.

(2) The saponification of ethyl sodium succinate. For details, which are rather scanty, *cf.* Mellor, pp. 101 *seq.*

Probably the most interesting types of consecutive reactions are to be found in radioactive changes, as already mentioned. These strictly belong to *heterogeneous* reaction velocities, but may be considered here. We are here dealing with a long series of consecutive changes. If we look upon the expulsion of α rays (which when deprived of their charge are identical with helium), or if we regard the expulsion of β and γ rays as "chemical" reactions, we are here furnished with side reactions accompanying the consecutive changes. To illustrate in a

general way how the existence of such consecutive changes was indicated by abnormalities in the decay curves, we may take the case of isolated thorium X, which gives rise to thorium emanation (Rutherford and Soddy, *Trans. Chem. Soc.*, **81**, 837, 1898). A piece of platinum wire upon which was deposited some thorium X was seen to lose its activity (as measured by its capability of discharging an electroscope), the following figures indicating the rate. The initial activity is called 100.

Time in days.	Activity of Th X.
0	100
1	117
2	100
3	88
4	72
6	53
9	29.5
10	25.2
13	15.2
15	11.1

These data are plotted in the following diagram (Fig. 37a). It will be observed that a maximum is passed through in the region of the first day interval. This suggests that at least *one* new radioactive product has been formed from the thorium X. This has been identified as thorium emanation. The shape of the curve should be compared with that of the production of iodine obtained in the case of the action of $K_2S_2O_8$ on H_3PO_3 in presence of HI (Fig. 36). By means of the systematic examination of the decay curves of various products in turn, other radioactive changes can be detected. Cf. Fig. 37b, which illustrates the recovery of activity of radium salt (curve A) and simultaneously the decay of radium emanation (curve B). These combined produced a "humped" curve. (Rutherford and

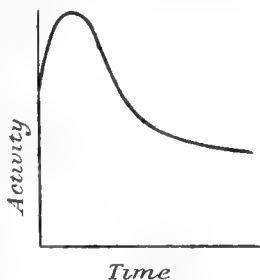


FIG. 37a.

Soddy, *Phil. Mag.*, [6] 5, 455, 1903). A curve which shows several humps points to the existence of, at least, a corresponding number of radioactive substances.

Initial Disturbance and Period of Induction.—These points may be raised at this juncture, since they are generally due to consecutive reactions, though there are other causes known which in certain cases will account for them. Any abnormality—such as that of variation in the velocity constant—which occurs in the earliest stages of a reaction, is called in general an initial disturbance. A period of induction is a particular type of initial disturbance in which we find that the combina-

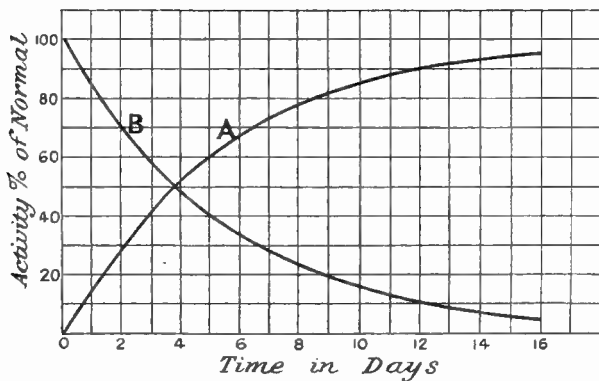


FIG. 37b.

tion or decomposition of a certain substance is delayed for a short period of time. That is to say, the velocity curve, instead of falling steadily, remains horizontal for a time, and then becomes normal in behaviour. The phenomenon of induction period was first observed by Cruikshank in 1801, who noted that the combination of hydrogen and chlorine did not proceed very rapidly until the mixture had been exposed to the light for some time. Bunsen and Roscoe named this stage of retardation in velocity the period of induction. Such abnormality may be ascribed roughly to three causes—

- (1) Presence of consecutive reactions.
- (2) The existence of passive resistances, *i.e.* something

which prevents the reaction starting off at full speed, but about which we know nothing, the term being simply an expression for lack of information.

(3) Autocatalysis, which we shall consider later on, in discussing homogeneous catalysis in general.

C. OPPOSING REACTIONS.

Opposing reactions result in chemical equilibrium, as determined by the law of mass action. We have already discussed the question of such equilibrium in homogeneous systems at considerable length. It will be remembered that the equilibrium constant K is simply the ratio of the velocity constants k_1 and k_2 of the opposing reactions. It will also be remembered that in dealing with the indirect method of determining K it was stated that K might be determined by measuring k_1 and k_2 for each reaction at a very early stage in each case, in fact the so-called initial velocity stage. Thus, if we take the familiar reaction—



(*hydrochloric acid being used as a catalyst*) and use Knoblauch's data (*Zeitsch. physik. Chem.*, **22**, 268, 1897), we find, starting with ester and water, the following data. Experiments carried out at 25° C.

t minutes.	Quantity of acid formed.	$\frac{\delta \text{ acid}}{\delta t}$.
0	0.0	—
78	0.0777	0.000966
86	0.0862	0.001003
94	0.0930	0.000989
		Mean = 0.000996

Similarly starting with acid and alcohol.

<i>t</i> minutes.	Quantity of ester formed.	$\frac{\delta \text{ ester}}{\delta t}$.
0	0	—
44	0.1327	0.00302
53	0.1628	0.00307
62	0.1847	0.00298
		Mean = 0.00303

The ester + water solution was prepared so as to contain 1 mole of ethyl acetate + 12.215 moles of water in a liter.

The initial velocity constant k_1 of acid and alcohol formation is then given by the expression—

$$\frac{dx}{dt} = k_1 \times \text{initial } C_{\text{ester}} \times \text{initial } C_{\text{water}}$$

$$\text{or} \quad 0.000966 = k_1 \times 1 \times 12.215$$

$$\therefore k_1 = 0.0000815$$

$$\text{and} \quad k_2 = 0.000238$$

$$\text{and hence} \quad \frac{k_2}{k_1} = K = 2.92$$

$$K \text{ observed} = 2.84 \text{ (after 24 hours)}$$

(possibly too short a time).

Knoblauch points out that Berthelot's value for K is 4 (over a fairly wide temperature range in the absence of hydrochloric acid), and ascribes the difference from his own as due to the hydrochloric acid; see, however, the later work of Jones and Lapworth (*Trans. Chem. Soc.*, 99, 1427, 1911), on the "removal" of water from the system by the hydrochloric acid, already discussed in dealing with homogeneous equilibrium, thereby giving values for K *higher* than 4.

The above method cannot, however, be strictly accurate, for at any stage of the reaction—and therefore, of course, even at the earliest—the correct expression for the rate of change is—

$$\frac{dx}{dt} = k_1(a-x)(b-x) - k_2x^2$$

where a and b are the original amounts of ester and water present, and hence the rate of decrease of ester, for example, is not characterised by a factor k_1 , but by $(k_1 - k_2)$.

For the present, instead of further studying these bimolecular and opposing reactions, let us consider an example of two opposing monomolecular reactions, namely, the conversion of hydroxybutyric acid into the corresponding lactone. This is carried out in solution in the presence of H^+ ions as catalyst; the H^+ ions at the same time act to make the hydroxybutyric acid assume a practically unionised state. The reaction velocity is thus—

$$\frac{dx}{dt} = k_1(a - x) - k_2x$$

where a is the initial amount of hydroxybutyric acid, and x the quantity transformed into lactone at the time t .

If the equilibrium constant is K —

$$K = \frac{k_1}{k_2}$$

Then

$$\begin{aligned} \frac{dx}{dt} &= k_2\{Ka - x(K + 1)\} \\ &= k_2(K + 1)\left(\frac{Ka}{K + 1} - x\right) \end{aligned}$$

and since

$$\frac{dx}{dt} = \frac{-d\left(\frac{Ka}{K + 1} - x\right)}{dt}$$

$$\therefore \frac{-d\left(\frac{Ka}{K + 1} - x\right)}{\left(\frac{Ka}{K + 1} - x\right)} = k_2(K + 1)dt \text{ or } (k_1 + k_2)dt$$

and hence on integrating—

$$-\log\left(\frac{Ka}{K + 1} - x\right) = (k_1 + k_2)t + \text{constant}$$

$$\text{where } t = 0 \quad x = 0 \quad \therefore \text{constant} = -\log \frac{Ka}{K + 1}$$

$$\therefore \frac{1}{t} \log \frac{\frac{Ka}{K+1}}{\frac{Ka}{K+1} - x} = k_1 + k_2$$

or
$$k_1 + k_2 = \frac{1}{t} \log \frac{Ka}{Ka - (K+1)x}$$

This expression was verified by Henry as follows:—

K was found at 25° C. = 2.68

<i>t</i> minutes.	<i>x</i> .	Value of $\frac{1}{t} \log \frac{Ka}{Ka - (K+1)x}$.
21	2.39	0.0411
50	4.98	0.0408
80	7.14	0.0444
120	8.88	0.0400
220	11.56	0.0404
320	12.57	0.0398
47 hours { equilibrium reached	13.28 { used for K calculation	—

Another example of monomolecular opposed reactions is to be found, in adding a small quantity of acetic acid to a concentrated solution of water and alcohol, whereby, of course, ethyl acetate is formed, but the alcohol and water concentration may be regarded as constant, so that the reaction is virtually acid \rightleftharpoons ester, and the equation is—

$$\frac{dx}{dt} = k(a - x) - k'x_2$$

where *a* is the amount of acid present initially, and *x* is the amount transformed into ester.

The same reaction, as already pointed out, is bimolecular, when no component is present in excess. Thus, if one mole of ester + one mole of water are present to start with, then at time *t*—

$$\frac{dx}{dt} = k_1(1 - x)^2 - k_2x^2$$

and
$$\frac{k_1}{k_2} = \frac{1}{4} \text{ (Berthelot and Pean de St. Gilles)}$$

so that on integration we obtain—

$$\frac{4}{3}(k_1 - k_2) = \frac{1}{t} \log \frac{2-x}{2-3x}$$

This equation is found to agree with facts, *i.e.* the right-hand side of the equation does really give a constant, viz. $\{\frac{4}{3}(k_1 - k_2)\}$.

Knowing $k_1 - k_2$ and also $\frac{k_1}{k_2}$, it is easy to determine k_1 and k_2 separately.

EFFECT OF TEMPERATURE ON VELOCITY.

From the kinetic standpoint of reaction velocities we might expect that the rate of reaction would depend on the number of collisions between the molecules in unit time, and hence if we could calculate from the kinetic theory the increase in collisions per degree rise in temperature, we would have obtained the value of the increase of the reaction velocity constant, due to temperature. The kinetic theory of gases leads to the following expression (Meyer, *Kinetic Theory of Gases*, translated by Baynes, p. 168):—

$$\text{Frequency of collision} = \left(1 + \frac{c}{T}\right) \sqrt{2\pi s^2} \frac{\Omega}{\lambda^3}$$

where πs^2 is the cross-section of the molecular sphere of action, Ω is the arithmetical mean molecular speed (a quantity which differs slightly as far as numerical values are concerned from the root-mean-square velocity, which appears in the kinetic energy expressions which define the temperature of the system), λ^3 is the volume "region," which contains one molecule. The term $\left(1 + \frac{c}{T}\right)$ takes into account the cohesive forces existing

between the molecules. Now the term $\left(1 + \frac{c}{T}\right)$ decreases as the temperature rises, and Ω increases as the temperature increases, so that on the whole the frequency of collision may or may not increase with temperature. Let us consider, however, the limiting case, *i.e.* the maximum variation in collisions to be expected by change in temperature. This can be accomplished by omitting the cohesion term, and

making frequency $\propto T$. On this assumption one can easily see that if we raise the temperature from 273° abs. to 283° abs., we increase the number of collisions per second to the extent of 2 per cent. But it has been found that, as a very approximate average, a rise of 10° causes the reaction velocity to double or treble itself, *i.e.* an increase of 200 per cent. to 300 per cent. It is therefore clear that some very large effect is coming in, which is not taken into account at all by the kinetic theory. Physical changes in general, such as viscosity, will not account for it. For this reason Arrhenius put forward the hypothesis of the existence of two types of molecules, active and passive, with an equilibrium existing between them. Let us take the case of cane sugar in water. The number of "active" molecules is supposed to be very small compared to the number of "passive" ones present. On raising the temperature, the equilibrium between these two kinds is supposed to shift over very rapidly, so that not only have we an increased collision frequency, but still more, we have a largely increased number of active molecules ready to take part in the reaction. It must be confessed that the assumption is rather *ad hoc*, but nothing better has as yet been suggested. (See, however, a paper by Lamb and Lewis (*Trans. Chem. Soc.*, 1915) for a physical treatment of the problem.)

In connection with the effect of temperature on the equilibrium constant K of a reversible reaction, van 't Hoff deduced on thermodynamical grounds the following relation:—

$$\frac{d \log K}{dt} = \frac{Q}{RT^2}$$

where Q is the heat absorbed per gram-molecule in the reaction, R is the gas constant, and T the absolute temperature. Now K may be written $\frac{k_1}{k_2}$, where k_1 and k_2 are the velocity coefficients for the direct and reverse reactions. So that the van 't Hoff relation becomes—

$$\frac{d \log \frac{k_1}{k_2}}{dt} = \frac{Q}{RT^2}$$

and if we make the assumption that throughout the range of temperature investigated, Q is constant, we find on integration—

$$\log K_{T_2} - \log K_{T_1} = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

or
$$\log \left(\frac{k_1}{k_2} \right)_{T_2} - \log \left(\frac{k_1}{k_2} \right)_{T_1} = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

This, however, only connects the difference of the logs of the ratios of the opposing velocity constants with the temperature. It does not give us the effect of temperature on the separate velocity constants, or on the velocity constant of an irreversible reaction, which goes practically to an end. It has been found, however, that the following empirical relation holds good (Arrhenius, *Zeitsch. physik. Chem.*, 4, 226, 1889) for "irreversible" reactions at different temperatures, viz.—

$$k_{t_2} = k_{t_1} e^{A \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

which is evidently—

$$\log \frac{k_{t_2}}{k_{t_1}} = A \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

it thus bears a formal resemblance to the van 't Hoff equation for variations in the equilibrium K . By way of illustration of this, one may quote the results of Spohr (*Zeitsch. physik. Chem.*, 2, 195, 1888) on the rate of inversion of cane sugar—

temperature, centigrade.	k calculated.	$A = 12,820.$ k observed.
25	(9.67)	9.67
40	75.7	73.4
45	144	139
50	(268)	268
55	491	491

The following table illustrates the same expression applied to the case of the saponification of ethyl acetate by NaOH

(Warder, *Amer. Chem. Journ.*, 3, 203, 1881; *Ber. d. deutsch. Chem. Gesell.*, 14, 1365, 1881):—

temperature, centigrade.	k calculated.	$A = 5579$. k observed.
3.6	1.48	1.42
5.5	1.70	1.68
7.2 = t_1	(1.92)	1.92
11.0	2.51	2.56
12.7	2.82	2.87
19.3	4.38	4.57
20.9	4.86	4.99
23.6	5.78	6.01
27.0	7.16	7.24
28.4	7.81	8.03
30.4	8.82	8.88
32.9	10.24	9.87
34.0 = t_2	(10.92)	10.92
35.0	11.60	11.69
37.7	13.59	13.41

Warder himself employed an empiric formula of a different type, which agreed with the data about as well as that given. Warder's formula may be put in the form—

$$k = A + BT^2$$

i.e. the velocity constant is put proportional to the square of the absolute temperature.

Arrhenius has applied his hypothesis of active and passive molecules to show how one may arrive at the expression—

$$\log \frac{k_{t_2}}{k_{t_1}} = A \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

It will be evident, however, that the "proof" does not rest on very solid ground.

Suppose we denote the equilibrium constant between active and passive molecules by the symbol X , then it follows as a particular case of the van 't Hoff theorem—

$$\frac{d \log X}{dt} = \frac{q}{RT^2}$$

where q denotes the heat absorbed in converting one gram mole from the passive into the active state. Let us assume

that q is constant over a fairly wide temperature range. $\frac{q}{R}$ can then be written A , and on integrating—

$$\log \frac{X_{T_2}}{X_{T_1}} = A \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Now Arrhenius assumes that in a solution (of cane sugar, for example) there is only a small fraction of active molecules, the equilibrium being

$$X = \frac{C_{\text{active}}}{C_{\text{passive}}}$$

If C_{active} is very small we can write as an approximation $C_{\text{passive}} = \text{total } C_{\text{sugar}}$, and doing this at two temperatures for the same total C_{sugar} , and also putting the reaction velocity constants k_{T_1} and k_{T_2} proportional to the quantities of the “active” molecules, we obtain—

$$\begin{aligned} k_{T_1} &= Y C_{\text{active}} = Y X_{T_1} C_{\text{passive}} = Y X_{T_1} C_{\text{sugar}} \\ k_{T_2} &= Y C_{\text{active}} = Y X_{T_2} C_{\text{passive}} = Y X_{T_2} C_{\text{sugar}} \end{aligned}$$

(where Y is a proportionality constant, supposed to be independent of temperature). Hence

$$\frac{k_{T_2}}{k_{T_1}} = \frac{X_{T_2}}{X_{T_1}} \text{ or } \log \frac{k_{T_2}}{k_{T_1}} = \log \frac{X_{T_2}}{X_{T_1}} = A \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Note that A in this case contains q , the heat of transformation from inactive to active molecules. It has nothing to do with the heat of transformation Q involved in the further chemical reaction, say of cane sugar into dextrose + lævulose. This must be clearly remembered, viz. that the variation of the velocity constant with temperature can, so far, be referred only to what is little more than an empiric relation. The measurement of the heat of the reaction Q does not allow us to calculate the velocity constant, for the relation $\frac{d \log K}{dt} = \frac{Q}{RT^2}$, which is absolutely sound, has reference only to the ratio of *opposing* velocities, at different temperatures, as has been already pointed out.

INFLUENCE OF PRESSURE ON REACTION VELOCITY.

In gaseous systems, the effect of increased pressure, if it brings about a volume change, will evidently increase the concentration terms, and the reaction will thereby go more rapidly. This effect has been considered in dealing with equilibrium in gaseous systems. In liquid systems the case somewhat resembles that of temperature influence, in that we know the effect of pressure on the *equilibrium* constant, viz.—

$$\frac{\partial \log K}{\partial p} = \frac{-\Delta v}{RT}$$

but this expression, again, only gives us the difference of the ratios of two velocity constants at different pressures. The above expression will be taken up later from a thermodynamic standpoint. Owing to the great incompressibility of liquids, this effect must be exceedingly small, and practically no work has been done upon the subject.

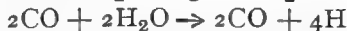
CATALYSIS IN HOMOGENEOUS SYSTEMS.

Positive Catalysis of Reactions.—First of all let us consider gaseous systems. It has been known for a long time (Dixon, 1880) that reactions between two gases such as carbon-monoxide and oxygen will not take place unless water vapour is present. The reaction may be written simply—

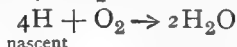


but this, of course, does not bring the water into play at all. Dixon virtually restated a proposition which had been put forward in 1794 by Mrs. Fulhame, namely, that the reaction takes place in two stages.

(1) CO reacts with H_2O to give CO_2 and nascent H



and (2)



The water, therefore, causes the formation of the intermediate substance, nascent hydrogen. Dixon showed the probability

of such a cycle of changes by demonstrating that H_2 is liberated from a heated mixture of carbon monoxide and steam, and also that hydrogen combines with oxygen to reform steam. Dixon further showed that other gases, such as sulphuretted hydrogen, ethylene, ammonia, pentane and hydrochloric acid, will cause CO and O_2 to unite; while sulphur dioxide, carbon bisulphide, cyanogen, carbon tetrachloride have no catalytic effect. Hence Dixon came to the conclusion that not only steam but all substances which will form steam under the conditions of the experiment, will cause carbon monoxide and oxygen to unite. This work may be regarded as demonstrating the intermediate compound view of catalysis.

Other reactions, however, occur in which it is difficult to assume the formation of an intermediate compound—such, for example, as the union of H_2 and Cl_2 under the action of light, which belongs to the section on Photochemistry. In fact, no general theory of homogeneous catalysis has yet been put forward. An attempt in this direction has been recently made by the writer and Mr. Lamble (*Trans. Chem. Soc.*, 1914, 1915). Each particular reaction so far has been examined *per se*, and in many cases the idea of an intermediate compound being formed, has been found to give a reasonable account, at least, of the facts. These conclusions hold equally well for catalysis in solutions, to which reference will now be made.

The most active catalytic agents in solution are H^+ and OH^+ ions. We have already met with the effects of these, *e.g.* the catalytic effects of H^+ ions on the inversion of cane sugar, or on the rate of hydrolysis of esters (by acids) in which, for dilute solutions of the catalysing H^+ ions, the velocity of the reaction is directly proportional to the H^+ ion concentration. For more concentrated solutions, however, this is not strictly accurate. The effect has been ascribed to H^+ ions, because the catalysis by different acids at equivalent concentration—provided that this is not too strong—is the same. Further, if the dissociation of the catalysing acid is thrown back, say by the addition of a soluble neutral salt of the acid, the catalytic effect is also proportionally decreased

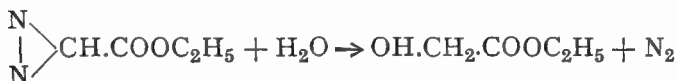
provided the acid is a weak one; if it is strong the catalytic effect actually increases. This will be discussed later. It will be remembered that Wij's method for obtaining the ionisation constant of water by the aqueous saponification of methyl acetate is based on the catalytic effect of the H^+ ion and the direct stoichiometric action of the OH' , the OH' ion in this case being 1400 times more effective than H^+ for the same concentration. Besides the intermediate compound theory mentioned above to account for catalytic processes, the view has also been put forward that the catalyst—by some unknown process—increases the number of active molecules at the expense of the passive ones. This evidently assumes the applicability of Arrhenius' hypothesis, which he brought forward to explain the effect of temperature. It is, of course, not a thorough explanation, since even granting the existence of active and passive molecules, the mode of increasing the number of active molecules is left unexplained, unless indeed we again fall back on the intermediate compound view. H. Euler (*Zeitsch. physik. Chem.*, 36, 405, 641, 1901) considers that all reactions are ionic in character, and hence he defines a catalyst as a substance which increases the concentration of the reacting ions—without, however, explaining *how*. Since catalysts, such as those mentioned above, take no permanent part in many of the reactions which they catalyse, they cannot effect the equilibrium point finally reached.¹ This must mean—since the equilibrium constant K is simply the ratio of the opposing velocities—that a catalyst affects both the direct and reverse reaction velocities to the same fractional amount. In fact, this was used as the criterion for the catalytic process. It has been shown, however, that in the majority of cases, not only does the catalyst act as such, but it likewise disappears to a certain extent, owing to its having participated in the reaction in a "secondary" manner. In such cases it is evidently possible that the equilibrium point may be shifted by the addition of the catalyst. Hence the most general criterion for a catalytic effect is that one (or more) of the substances does not react

¹ Koelichen, *Zeitsch. physik. Chem.*, 33, 149, 1900.

according to any simple stoichiometric equation. In fact, when we cannot state definitely the exact function of one of the constituents which takes part in a reaction, we put it down to catalytic effects. In other words, catalysis is a term for unsolved mechanism. In connection with ionic catalyses in solution, mention should be made of the peculiar effect known as neutral salt action. If we take a reaction which is catalysed by the H^+ ions of an acid, and add, say, the sodium salt of the acid, then if the acid is a weak one, the catalytic effect will be decreased as already pointed out. But besides this effect, which is to be expected on the dissociation theory, we sometimes find an increase in the velocity—evidently due to specific catalysing properties possessed by the undissociated molecule of the acid. Thus Mellor, *Statics and Dynamics*, p. 280, quotes the case of cane sugar catalysed by 0.05N HNO_3 , which gives the velocity constant 29.9; the addition of 0.4N KNO_3 raises the velocity to 33.9 instead of lowering it to 27.2. All ions have probably a catalytic effect, though H^+ and OH' are quite unique in this respect. It is rather suggestive that the ions which form the solvent—for the great bulk of reactions have been studied in aqueous solution—are those which are most catalytically active. It is not improbable that the solvent itself plays a considerable part in every reaction in solution, and that the H^+ and OH' ions assist this by continuously alternating ionisation and reformation of H_2O molecules. Having discussed homogeneous catalysis in general terms, it is of interest to make ourselves acquainted with some of the more specific cases (*cf.* Bredig, "Altes und Neues von der Katalyse," *Biochem. Zeitsch.*, 6, 283, 1907). The first instance of measurements of catalysis by OH' ions by kinetic methods was the transformation of atropine into hyoscyamine, which occurs when a little alkali or other base is added to the system (W. Will and G. Bredig, *Ber.*, 21, 2777, 1888). The same catalytic agent causes the partial transformation of glucose, mannose, and fructose into one another,¹ and the transformation of diacetone alcohol into acetone, Koelichen (*loc. cit.*). The catalytic action of H^+

¹ Lobry de Bruyn and von Ekenstein.

ion has been found to be present in a still larger number of cases. Mention has already been made of the sugar inversion and ester saponification. Besides these, the H^+ ion acts catalytically in the hydrolysis of lactones, and in the formation of anilides and esters (*cf.* H. Goldschmidt, to whose work we shall refer later), the intramolecular change in diazo-amido compounds, and especially the decomposition of diazoacetic ester, which has formed the subject of an extensive series of researches by Prof. Bredig and his pupils. Some of the numerical results obtained in the diazoacetic ester decomposition may be of interest. This ester is decomposed by water, as Curtius showed in 1883, according to the equation—



Fraenkel, under Bredig's direction (*Zeitsch. physik. Chem.*, 1907), showed that the rate of decomposition of the diazo ester in aqueous solution containing acid was proportional to the concentration of H^+ ions, as is shown by the following table:—

Catalysing acid.	Concentration of acid in gram molecules per liter.	C_H .	Monomolecular velocity constant k at 25° for diazo ester decomposition.	Proportionality factor between H^+ and k , viz. $F = \frac{k}{C_H}$.
Nitric . . .	0·00182	0·00182	0·0703	38·7
	0·000909	0·000909	0·0346	38·0
Picric . . .	0·000909	0·000909	0·0356	39·2
	0·000364	0·000364	0·0140	38·3
<i>m.</i> nitrobenzoic	0·00990	0·00168	0·0632	37·7
Fumaric . .	0·00364	0·00146	0·0571	39·1
Succinic . .	0·00909	0·000724	0·0285	38·5
Acetic . . .	0·0182	0·000563	0·0218	38·7
Mean				38·5

The rate of the reaction was simply determined by reading at given times in a burette the amount of gas (N_2) given off from the solution, which was kept vigorously stirred to prevent supersaturation. The above data show that we are dealing

with a simple H^+ ion catalysis. This is further shown by the effect produced by the addition of sodium acetate to the solution, which contained acetic acid as catalyst. Assuming the validity of the dissociation theory regarding "ionic product," one can calculate the quantity of H^+ ion in each case in presence of the sodium acetate. The following data were obtained :—

Concentration of acetic acid.	Concentration of sodium acetate.	C_{H^+} (calculated).	Velocity constant k at 25° .	$F = \frac{k}{C_{H^+}}$.
0.0909	0	0.00127	0.0500	39.4
	0.00227	0.000584	0.0234	40.0
	0.00455	0.000351	0.0144	40.9
	0.00909	0.000192	0.0008	41.7
0.0182	0.000909	0.000276	0.0109	39.3

This diazo ester decomposition is a very delicate quantitative test for H^+ ion. Walker and his pupils have used it to determine the H^+ ion concentration in solutions of amphoteric electrolytes, such as glycoll ($NH_2 \cdot CH_2 \cdot COOH$) which acts both as a base and as an acid in virtue of the simultaneous presence of NH_2 and $COOH$ groups. The same method has also been employed by Bredig and Spitalsky (*Zeitsch. anorg. Chem.*, **54**, 265, 1907) to determine the extent of hydrolysis of potassium bichromate, which gives rise to chromic acid, which may be determined by the estimation of the H^+ ion concentration.

Besides H^+ ion and OH^+ ion catalyses other ions are effective, though in general to a less extent. Thus Bredig and Walton (*Zeitsch. physik. Chem.*, **47**, 185, 1904) have examined the catalytic effect of the iodine ion I^- , on the decomposition of H_2O_2 in aqueous solution. Equivalent solutions of sodium iodide, potassium iodide, and ammonium iodide were found to accelerate the reaction to the same extent, whereas cadmium iodide at the same equivalent concentration was much less effective, which is in agreement with the known fact that cadmium iodide forms complex ions in solution, as well as

giving rise to I' ions. Some of the results obtained are as follows:—

Catalyst.	Concentration of catalyst in equivalents per liter.	Velocity constant k_{25} (monomolecular).	$F = \frac{k_{25}}{C_{\text{catalyst}}}$.
KI . .	0.00699 0.03684	0.00945 0.04761	1.35 1.29
NaI . .	0.00616 0.03678	0.00813 0.04810	1.31 1.32
NH_4I . .	0.02656 0.03947	0.0357 0.0529	1.35 1.34
$\frac{1}{2}CdI_2$. .	0.00976 0.0842	0.00947 0.0453	0.97 0.54

The catalytic effect can be stopped by adding iodine (I_2), which converts I' ion into inactive I'_3 , or by adding mercuric iodide, which forms a complex anion. The mechanism of the reaction, from the standpoint of the intermediate compound theory of catalysis, is represented thus—

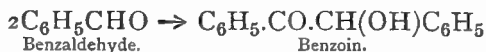
Slow reaction (1) $H_2O_2 + I' \rightarrow H_2O + IO'$ (anion of hypoiodous acid)

Fast reaction (2) $H_2O_2 + IO' \rightarrow I' + O_2 + H_2O$

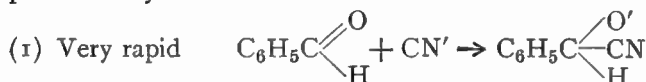
or summing both $2H_2O_2 \rightarrow 2H_2O + O_2$

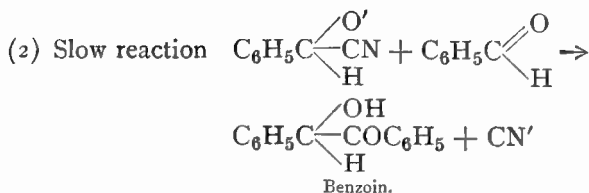
The dichromate ion $Cr_2O_7^{--}$ was also shown to have a similar effect on the same reaction.

Bredig and Stern (*Zeitsch. physik. Chem.*, 50, 513, 1905) also investigated the catalytically active CN' ion in the well-known reaction—



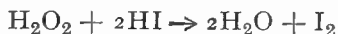
which takes place in the presence of potassium cyanide, sodium cyanide or barium cyanide. The reaction is a bimolecular one, and the velocity constant depends on the quantity of CN' ion present. The mechanism of the reaction is represented by—





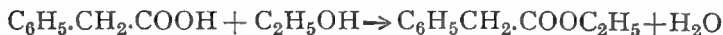
In support of this it has been shown that the conductivity of potassium cyanide solution is diminished by the addition of benzaldehyde, thereby pointing to the formation of a compound.

Another well-known instance of catalysis is the effect of a small quantity of ferrous sulphate or molybdic acid on the reaction—



One-millionth of a mole of molybdic acid per liter doubles the velocity constant of the reaction.

Autocatalysis.—Mention has already been made of H. Goldschmidt's work on ester formation and the catalytic effect of H^+ ions. That the effect is really due to these ions is shown by the following results (*Ber.*, 29, 2208, 1896). Phenyl acetic acid was dissolved in ethyl alcohol, the solution being (0.2372)N. The reaction is—



Since the alcohol is in large excess the reaction should be monomolecular. To obtain measurable velocities, picric acid was added, the particular concentration of this acid in Experiment I. being 0.01 N. Temperature 35°C . In Experiment II., a salt of picric acid, namely, *p*-toluidine picrate (0.01 N) is added so that the dissociation of the picric acid may be thrown back, and if the catalytic effect is due to the H^+ ions, the velocity constant for the phenyl-acetic esterification should be decreased. In Experiment III. the same substances are present as in II., the *p*-toluidine picrate being, however, 0.02 N.

I. $k = 0.0187$; II. $k = 0.0086$; III. $k = 0.0072$

(The values for the constant in each case fall as time goes on, especially in I.)

Having established by the above and many other measurements, that H^+ ion does accelerate the rate of ester formation, it is evident that this effect must come in even when we add no catalysing acid, but simply from the hydrogen ions of the acid itself which is being gradually esterified. This is called autocatalysis. At any moment for a monomolecular reaction catalysed by an ion, and proportionately to the concentration of the ion, we have—

$$\frac{dx}{dt} = k(a - x)C_{ion}$$

$(a - x)$ is *total acid* (dissociated and undissociated) present at any moment.

When the catalysing ion, *i.e.* the H^+ ion, is produced from the acid which is being esterified (no other catalyst being added) the concentration of the H^+ ion is a function of the time, being at any moment identical with the amount of dissociated unesterified acid, *viz.* $(a - x)m$, where m is the degree of dissociation of the acid. Hence in such a reaction we have—

$$\frac{dx}{dt} = k_1(a - x)^2m$$

which has the form of a bimolecular reaction. Supposing m remains constant throughout the range examined, *i.e.* if measurements are made while the absolute concentration of the acid is not altered much, we can integrate the expression putting—

$$k_1m = k_{25^\circ}$$

whence

$$k_{25^\circ} = \frac{1}{t} \cdot \frac{x}{a(a - x)}$$

The approximate applicability of this expression is shown in the subjoined table, the values given by making use of the monomolecular expression being added for comparison—

<i>t</i> hours.	<i>a</i> = 12.06 (c.c. of titrating alkali).		
	<i>a</i> - <i>x</i> .	$\frac{1}{t} \log \frac{a}{a-x}$.	$\frac{1}{t} \frac{x}{a(a-x)}$.
47.8	11.18	0.000685	0.00676
118	10.24	0.000601	0.00626
191	9.24	0.000605	0.00663
291	8.30	0.000557	0.00648
407.5	7.50	0.000506	0.00618
554	6.58	0.000475	0.00622
672	6.07	0.000444	0.00605

These results and others not quoted are very much in favour of the applicability of the bimolecular formula, though the fall in the value of the constant with time shows that some secondary influence¹ is at work. The assumption that *m* is constant can scarcely be accurate when the range is as wide as that given, viz. total acid concentration falls from 12.06 to 6.07, though the fact that the reaction is taking place in alcohol solution means that the dissociation is small, and possibly not very variable even over this range. (For Donnan's criticism, *cf. Ber.*, 29, 2422, 1896.)

On the assumption that *m* is practically constant (and therefore Ostwald's expression $K(1-m) = m^2(a-x)$ is inapplicable) one sees that a bimolecular reaction will be given by one of three processes.

(1) If the reaction takes place between the undissociated molecules only—

$$\frac{dx}{dt} = k(1-m)(a-x)$$

and it is necessary to assume autocatalysis to obtain the bimolecular reaction—

$$\frac{dx}{dt} = k(1-m)m(a-x)^2$$

¹ The influence referred to is probably due to the water formed in the reaction; *cf.* the section dealing with catalytic effects of the solvent.

(2) If total acid reacts and there is catalysis (m constant)—

$$\frac{dx}{dt} = k(a - x)^2m$$

i.e. bimolecular (Goldschmidt's case).

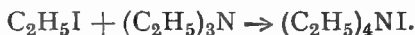
(3) If the reaction takes place between the alcohol and the ions of the acid,

$$\frac{dx}{dt} = km^2(a - x)^2$$

which is bimolecular and does away with the possibility of autocatalysis, for autocatalytic effects would produce a tri-molecular reaction. Hence to decide whether autocatalysis is present or not, it is necessary to know whether it is the ions of the acid, or the undissociated portion which reacts, and whether m is to be regarded as constant or not. Since we know that H' ion added "artificially" catalyses the reaction, it seems very reasonable at least to believe that autocatalysis must be present in the above case.

CATALYTIC INFLUENCE OF THE MEDIUM ON CHEMICAL VELOCITY.

The relative influence of isolated solvents is shown by the following results taken from the work of Menschutkin (*Zeitsch. physik. Chem.*, 6, 41, 1890) on the action of ethyl iodide on triethylamine—



The reaction occurred as a simple bimolecular one, the velocity constant having the following values :—

Solvent.	Velocity constant.	Dielectric constant of solvent.
Xylene . . .	0.00287	2.6
Benzene . . .	0.00584	2.6
Ethyl alcohol .	0.0366	21.7
Methyl alcohol .	0.0516	32.5
Acetone . . .	0.0608	21.8
Benzyl alcohol .	0.1330	10.6

The velocity in benzyl alcohol is more than twenty times greater than in benzene, for example. It will be noted that the series of velocity constants follows approximately the series of dielectric constants for the solvents, but the rule is by no means general. It suggests that electrical effects are at the basis of the reaction, *cf.* the Nernst and Thomson rule. A striking contradiction of the rule is, that the velocity of the transformation of ammonium cyanate into urea is thirty times as fast in *ethyl alcohol* as in *water*, although the dielectric constant of water is four times as great as that of ethyl alcohol. The reaction velocity, therefore, is not to be referred to the physical properties of the solvent alone; the velocity is rather a specific chemical property of the reacting substances. An attempt has been made to find a connection between reaction velocity and the viscosity of the medium. That viscosity changes cannot account by any means for the whole effect is seen at once when one remembers the extraordinary large differences in reaction velocity, occurring in solvents such as benzene and benzyl alcohol, where the viscosities are not very different. One may also draw attention to the work of L. Bruner and his pupils (*Bulletin de l'Academie des Sciences de Cracovie*), during the last few years on the effect of the solvent as determining the relative amounts of ring and side chain products formed, in the bromination of aromatic hydrocarbons. The conclusion arrived at, is that an ionising solvent such as nitrobenzene assists the substitution in the ring while a non-ionising (less ionising) solvent such as carbon bisulphide and carbon tetrachloride has the effect of assisting side-chain substitution.

Negative Catalysis in Homogeneous Systems.—By negative catalysis is meant the inhibiting action of certain substances on the velocity of a given reaction. Bigelow (*Zeitsch. physik. Chem.*, 26, 493, 1898), for example, showed that in the oxidation of sodium sulphite by oxygen in aqueous solution, the rate was much reduced by the presence, in very small quantities, of substances, such as mannite, benzyl alcohol, and benzaldehyde. Analogous cases occur in which ions are the retarding agents. The mechanism may be, as in the case of

positive catalysis, the formation of intermediate compounds, though practically nothing is known about the question.

As regards the kinetics of such reactions, Ostwald (*Allgemeine Chem.*, II, 2, 270) assumed that in the case of monomolecular reactions in which one of the products of the reaction had a retarding effect, *i.e.* we are dealing with *negative autocatalysis*, the expression for the velocity could be expressed as the difference of two terms, thus—

$$\frac{dx}{dt} = k_1(a - x) - x(a - x)$$

where x is the quantity of negative catalyst (or anticatalyst) produced at the time t . This expression has, however, been found not to hold good, and in Müller's experiments (*Zeitsch. physik. Chem.*, 41, 483, 1902) on the hydrolytic decomposition of bromo-succinic acid, the assumption is made that the rate of reaction is directly proportional to the amount of bromo-succinic acid left, *viz.* $(a - x)$, and inversely as the amount of anticatalyst (HBr), or—

$$\frac{dx}{dt} = k \frac{a - x}{x}$$

which was found to be in agreement with the results. Bodenstein (Review of Chemical Kinetics and Catalysis, *Zeitsch. Elektrochemie*, 15, 390, 1909) offers the same explanation for the remarkable result obtained by Lapworth (*Trans. Chem. Soc.*, 93, 2163, 2187, 1908) in the saponification of ethyl acetate by water in acetone solution, who found that the reaction, instead of being bimolecular as one would expect, was in reality independent of the water concentration, the expression—

$$\frac{dx}{dt} = kC_{\text{ester}} \quad \text{or} \quad \frac{1}{t} \log a \frac{a}{a - x} = k$$

being in satisfactory agreement with experiment. Water in organic solvents is known to have frequently an anticatalytic effect, and Bodenstein suggests the expression for the reaction velocity—

$$\frac{dx}{dt} = k \frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{water}}}$$

which evidently would explain Lapworth's result. Recently (*Trans. Chem. Soc.*, **99**, 1049, 1910) Senter and Porter have put forward a similar view of negative autocatalysis, the anti-catalyst being the hydrobromic acid formed in the hydrolytic decomposition of bromo-propionic acid in aqueous solution—

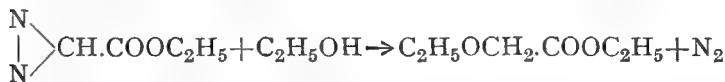


and the analogous anticatalytic effect produced by nitric acid in the reaction between certain bromine substituted aliphatic acids, and silver nitrate in alcoholic solution, the velocity equation in the latter case taking the form—

$$\frac{dx}{dt} = \frac{k(a-x)^2}{x}$$

Besides the cases of anticatalysis already mentioned, further attention must be paid to the anticatalytic effect of *water*, either when formed by the reaction itself or produced by actual addition to the system, the solvent in which the reaction occurs being one of the alcohols—usually ethyl alcohol.

Bredig's Investigations on Diazo Acetic Ester Decomposition in Alcoholic and Aqueous Alcoholic Solution.—Besides the decomposition of diazo acetic ester by water, its decomposition may also be effected by alcohol, and may take place in aqueous alcohol mixtures. In pure alcohol the reaction is—



This reaction is likewise hastened by acids. Employing picric acid as catalyst of molar concentration 0.009N, Millar (*Dissertation*, Heidelberg, 1910; cf. also Millar, Braune, and Snethlage's papers in the *Zeitsch. physik. Chem.*, **85**, 129 seq., 1913) found that in a pure alcoholic solution the velocity constant was 0.056. The dissociation of picric acid in ethyl alcohol is much less than in water. According to H. Goldschmidt,¹ it gives a dissociation constant in the former solvent,

¹ *Ber.*, **39**, 111, 1906.

viz. $k_{\text{Ostwald}} = 0.00058$, while it is known to be so strong an acid in aqueous solution that it gives none. Employing this value for the dissociation constant of the acid, it is found that a 0.009 molar solution is dissociated to the extent of 22.3 per cent., *i.e.* $C_{\text{H}^+} = 0.00203$, and hence the proportionality factor—

$$F' = \frac{k_{25}}{C_{\text{H}^+}} = \frac{0.056}{0.00203} = 28$$

This naturally differs from the factor F in aqueous solution as the reaction is of a different nature, *i.e.* it gives rise to the substance—



Starting with pure alcohol as solvent, and successively adding greater quantities of water, one would expect—since the dissociation of the catalyst (as far as increased conductivity results go) apparently steadily increases and also since the proportionality factor F , which one would think would come more and more into play, is greater than F' —that the velocity of decomposition of the ester should increase with increasing water addition (or decrease with increasing alcohol addition, supposing we started from the 100 per cent. water side). This latter case was realised by Fraenkel, as the following data show:—

Concentration of picric acid = 0.000909 mole per liter.

Grams alcohol in 100 grams of reaction mixture.	Velocity constant k_{25} .
0	0.0356
3.31	0.0320 (mean)
6.69	0.0288 — 0.0290
14.2	0.0202 — 0.0206
21.9	0.0133 — 0.0134

Starting from the pure alcohol side, however, Millar found that the addition of water caused a decrease in the velocity of decomposition, followed later by an increase, *viz.*—

Concentration of picric acid = 0.009 mole per liter.

Moles H ₂ O per liter	0	0.02	0.04	0.08	0.16	0.32	0.64
Velocity $k_{25} \times 10^3$	57	53	47	42	33	26	18
Moles H ₂ O per liter	1.28	2.56	5.12	10.24	15.36		
Velocity $k_{25} \times 10^3$	11	6.4	4.4	4.9	7.0		

The values of k_{25} pass through a minimum in the region of 6 moles of H₂O per liter = 11 per cent. water.

This unexpected and complicated behaviour has not yet received satisfactory theoretical treatment. It is considered by Bredig and his pupils as analogous to results obtained by H. Goldschmidt in the case of ester formation, in which the water formed in the reaction had an inhibitive effect. It is doubtful, however, if Goldschmidt's theory will apply to the diazo-ester case. (The whole problem of the diazo ester decomposition should be studied carefully by all interested in homogeneous catalysis. Besides the references given, cf. Bredig, *Verhandlung des Naturhistorisch-medizinischen Vereins zu Heidelberg*, N.F., 9, 1907.)

In the above case of diazo acetic ester decomposition, the change in the nature of the *solvent* has had a most marked effect on the rate of the reaction. Other similar instances are known, for example, the decomposition of oxalic acid, which in concentrated sulphuric acid solution decomposes according to the equation—



Bredig and Lichty (*Zeitsch. Elektrochemie*, 12, 459, 1906; *Journ. Phys. Chem.*, 11, 225, 1907) showed that even the slightest trace of water had a marked inhibitive effect, indeed, so marked that they put it forward as a method for determining traces of water in concentrated sulphuric acid. Thus, if 0.6 per cent. of water is present the reaction velocity constant is 0.018 at 70° C., while at the same temperature the presence of 3 per cent. water lowers the velocity constant to the value 0.00094; whether there is ionic catalysis here or not is unknown.

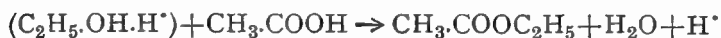
*H. Goldschmidt's Theory of Esterification of Acids.*¹—The most striking point in connection with the formation of ester from an acid—such as phenylacetic, acetic, propionic, butyric, etc.—dissolved in alcohol, is that an addition of water, even though in small quantities, exerts a depressing effect upon the velocity constant, though to a much less degree than in the case of diazo acetic ester decomposition. This behaviour is of importance because water is one of the products of the reaction itself, a special case of negative autocatalysis. Goldschmidt has attempted to account for this behaviour in the following way.

As regards the formation of possible intermediate compounds, we might assume that in aqueous and alcoholic solutions of H^+ ion, we have respectively ion hydrates ($H_2O.H^+$) and ion-alcoholates ($C_2H_5OH.H^+$). Now when H^+ (say from hydrochloric acid) is added for catalysing purposes to a pure ethyl alcoholic solution of acetic acid, we may suppose that in the first place a complex ion is formed, either between the acetic acid and the H^+ ion, *i.e.* ($CH_3.COOH.H^+$) or between the alcohol and the H^+ ion ($C_2H_5.OH.H^+$). The fact that the so-called hydrolytic constant r , to which we will refer in a moment, is practically independent of the nature of the acid undergoing esterification, is taken as evidence that the active catalytic agent is ($C_2H_5.OH.H$) and that one can neglect ($CH_3.COOH.H^+$) as probably not being formed at all. Further evidence that the active catalytic agent is ($C_2H_5OH.H^+$), and not an addition product with the acid undergoing esterification, was given later by Goldschmidt (*Zeitsch. Elektrochemie*, 15, 4, 1909). He showed that the *ratio* of the velocities of esterification of an organic acid, obtained when using hydrochloric acid and picric acid respectively as catalyst, was independent of the nature of the acid esterified.

¹ Goldschmidt and Udby (*Zeitsch. physik. Chem.*, 60, 728, 1907).

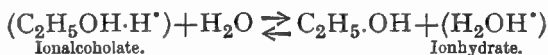
Velocity constant.	Acetic.	Propionic.	n.-Butyric.	Phenylacetic.
k in presence of $\frac{N}{10}$ HCl	2'179	1'544	0'764	0'902
k in presence of $\frac{N}{10}$ picric acid . . .	0'162	0'115	0'0582	0'655
Ratio $\frac{k_{\text{HCl}}}{k_{\text{picric}}}$. . .	13'5	13'1	13'1	13'8

Similarly, using hydrochloric acid and sulpho-salicylic acid as catalysts, a constant ratio analogous to the above is obtained. The same alcohol, of course, is used throughout. Goldschmidt assumes, in fact, that the velocity of esterification is directly proportional to the concentration of the alcoholate ($\text{C}_2\text{H}_5\text{OH}\cdot\text{H}^*$). The *free* H^* ion is assumed ineffective. The mechanism of esterification is therefore—



(The *total* H^* ion, *i.e.* the sum of the combined and free hydrogen ion, is therefore unchanged (theoretically)).

Now on the addition of water Goldschmidt assumes—and this is the kernel of his theory—that the following reaction occurs :—



this reaction comes to an equilibrium point very rapidly. Evidently the complex (H_2OH^*) has no esterifying power, in fact it is the complex which we would expect to saponify the ester, in ester saponification by catalytic H ion. Hence, if the above reaction takes place, the addition of water causes a decrease in the active esterifying agent ($\text{C}_2\text{H}_5\cdot\text{OH}\cdot\text{H}^*$), and hence the addition of water causes, *ceteris paribus*, the velocity to decrease. This explains, therefore, the inhibitive or anti-catalytic effect of water. If we denote by—

ξ = the equilibrium concentration of the ionalcoholate ($\text{C}_2\text{H}_5\cdot\text{OH}\cdot\text{H}^*$),

n = the concentration of the water added, *i.e.* the initial concentration,

x = the concentration of the water produced by the esterification,

x also denotes the quantity of acetic acid which has disappeared,

r = the equilibrium constant of the ionhydrate, ionalcoholate equilibrium; r is called by Goldschmidt, the hydrolytic constant,

η = equilibrium concentration of the ionhydrate ($\text{H}_2\text{O} \cdot \text{H}^+$), then, applying the law of mass action to the ion complexes equilibrium, we get—

$$\text{C}_{\text{C}_2\text{H}_5\text{OH} \cdot \text{H}^+} \times \text{C}_{\text{H}_2\text{O}} = r \text{C}_{(\text{H}_2\text{O} \cdot \text{H}^+)}$$

The constant r contains the value of $\text{C}_{\text{C}_2\text{H}_5\text{OH}}$, the solvent which may be regarded as constant for small additions of water, this being the limits of applicability of Goldschmidt's considerations. Hence in symbols—

$$\xi \times (n + x - \eta) = r\eta$$

$$\text{or} \quad \eta = \frac{n + x}{r + \xi} \xi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now consider the state of things before any water is added to the system at all. The concentration of the ionalcoholate ($\text{C}_2\text{H}_5\text{OH} \cdot \text{H}^+$) is ξ_0 . When water is added, and this complex is reduced to ξ , the concentration term η evidently represents the quantity of ($\text{C}_2\text{H}_5\text{OH} \cdot \text{H}^+$), which has disappeared in order to allow the formation of $\text{H}_2\text{O} \cdot \text{H}^+$. That is—

$$\xi_0 - \xi = \eta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

But if at the stage before water is added b denotes the concentration of the solvent, viz. alcohol (about 17 gram-moles per liter at $25^\circ \text{C}.$), and c the total concentration of H^+ of the catalysing acid,¹ we have for the reaction in which the active complex ($\text{C}_2\text{H}_5\text{OH} \cdot \text{H}^+$) is produced, viz.



¹ Goldschmidt denotes the total acid by C , in his paper with Udby, *Zeitsch. physik. Chem.*, **60**, 728, 1907. We may assume proportionality between the two.

the mass law relation—

$$\phi \cdot c \cdot b = \xi_0$$

where ϕ is the equilibrium constant.

Substituting this value of ξ in (2) we get—

$$\xi = \phi \cdot b \cdot c - \eta$$

or

$$\eta = \phi \cdot b \cdot c - \xi$$

and putting this value of η in (1) we obtain—

$$\xi = \phi bc - \xi \frac{n+x}{r+\xi}$$

or

$$\xi = \frac{1}{2} [\sqrt{(4\phi bcr) + (r+n+x-\phi bc)^2} - (r+n+x-\phi bc)] \quad (4)$$

Now at any stage of the reaction, *e.g.* when water is present, the rate of esterification is proportional to the concentration of the acid, *i.e.* acetic acid, *viz.* $(a-x)$, and also proportional to the concentration of the catalyst ξ . That is—

$$\frac{dx}{dt} = k(a-x)\xi$$

On substituting the value of ξ given by (4), and integrating, we obtain—

$$\begin{aligned} \frac{1}{2}kt = \frac{l+m}{q^2} \log \frac{Z_0+m-l}{Z+m-l} - \frac{l-m}{q^2} \log \frac{Z_0+m+l}{Z+m+l} \\ - \frac{2m}{q^2} \log \frac{Z_0}{Z} - \left(\frac{1}{Z} - \frac{1}{Z_0} \right) \cdot \cdot \cdot \quad (5) \end{aligned}$$

where—

$$q^2 = 4\phi bcr$$

$$m = a + r + n - \phi bc$$

$$l = \sqrt{(a+r+n-\phi bc)^2 + 4\phi bcr}$$

$$Z_0 = \sqrt{(r+n-\phi bc)^2 + 4\phi bcr} - (r+n-\phi bc)$$

$$Z = \sqrt{(x+r+n-\phi bc)^2 + 4\phi bcr} - (x+r+n-\phi bc)$$

A more simplified treatment of the problem is obtained if we neglect η (the concentration of (H_2OH^+)) compared with $n+x$, the actual quantity of water present. Thus equation (1) becomes—

$$\xi(n+x) = r\eta, \text{ or } \eta = \frac{\xi(n+x)}{r}$$

and since as before—

$$\eta = \phi b c - \xi$$

we obtain by combining these two expressions—

$$\xi = \frac{\phi b.c.r}{n+x+r}$$

and substituting this in the expression—

$$\frac{dx}{dt} = k(a-x)\xi$$

on integration we obtain—

$$kct = (n+r+a) \log \frac{a}{a-x} - x \quad . \quad . \quad (5A)$$

This latter equation applies fairly well when c and n are not too large. Goldschmidt used this form to determine r . Taking any two experiments with the same acid, and determining values of x , viz. x_1 and x_2 at times t_1 and t_2 , we obtain from (5A)—

$$t_2 \left[(r+n+a) \log \frac{a}{a-x_1} - x_1 \right] = t_1 \left[(r+n+a) \log \frac{a}{a-x_2} - x_2 \right]$$

which allows us to calculate r . With esterification of phenyl acetic acid, $r=0.151$; with acetic acid, $r=0.154$; with propionic acid, $r=0.146$; with monochloroacetic acid, $r=0.142$. The mean value of r , Goldschmidt takes to be, $r=0.15$, and since this value varies so little from acid to acid, he considers that the active complex formed by the H^+ ion of the catalyst, must be formed by the union of the H^+ ion with the alcohol, *i.e.* the active complex must be $(C_2H_5OH.H^+)$, as we have assumed throughout. Although, this conclusion, is reasonable, it is still open to question. As regards some numerical values, the following may be quoted for the esterification velocity of phenyl acetic acid, hydrochloric acid being the catalyst; t has the usual significance, and k_0 denotes the "constant," calculated as a simple monomolecular reaction, assuming the catalyst has constant activity independent of the water present, *i.e.* no allowance being made for anticatalysis. It will be observed that k_0 varies very much with the time;

k_c denotes the constant calculated from the simplified equation (5A). The constant is fairly good. K denotes the value obtained from the complicated equation (5). The constancy of this value is better than any of the other values, though even this value is not very good, when the water value n is in any way considerable. This is probably due to the fact that while Goldschmidt assumes the complex (H_2OH^+) to be quite inactive, its *saponifying* action is not negligible at the water concentration, $n = 0.8$ mole per liter.

ESTERIFICATION OF PHENYL-ACETIC ACID.

$a = 0.1.$	$c = 0.1.$	$n = 0.$	
t hours.	$k_0.$	$k_c.$	$K.$
0.104	0.854	0.314	52.2
0.304	0.803	0.322	52.4
0.504	0.758	0.320	50.9
0.903	0.707	0.322	52.0

$a = 0.1.$	$c = 0.1.$	$n = 0.1.$	
t hours.	$k_0.$	$k_c.$	$K.$
0.1	0.555	0.328	51.3
0.3	0.537	0.330	51.6
0.604	0.520	0.336	52.2
1.1	0.496	0.334	52.3

$a = 0.1.$	$c = 0.1.$	$n = 0.8.$	
t hours.	$k_0.$	$k_c.$	$K.$
0.307	0.149	0.327	48.5
1.5	0.125	0.278	47.2
3.0	0.116	0.267	39.6
6.0	0.111	0.265	38.7

$a = 0.1.$	$c = 0.2.$	$n = 0.8.$ ⁹	
t hours.	$k_0.$	$k_c.$	K.
0.25	0.282	0.622	47.7
0.60	0.279	0.621	47.4
1.25	0.274	0.616	46.9
2.50	0.262	0.603	46.4

Note that the constants decrease slightly with the addition of water, but the experimental error has a very large effect. See also Goldschmidt (*Zeitsch. physik. Chem.*, **70**, 627, 1910), also *Zeitsch. Elektrochemie*, **15**, 1909 (several papers).

It may be pointed out that the Goldschmidt theory will not account for the anticatalytic effect of water on the diazo acetic ester decomposition in the presence of H^+ ion in alcoholic solution, for the anticatalytic effect in Goldschmidt's case depends on the fact, that the complex H_2OH^+ can have no esterifying power, or has indeed probably a saponifying influence. On the other hand, the complex H_2OH^+ appears to be even more active as a decomposer of diazo acetic ester than the complex $(C_2H_5.OH.H^+)$, i.e. $F > F'$, and hence any formation of $(H_2O.H^+)$ at the expense of $(C_2H_5.OH.H^+)$ will cause an *increase* in the rate of the diazo acetic ester decomposition.

For a discussion of the kinetics of ferments—which produce both homogeneous and heterogeneous solutions, see V. Henri, *Lois générales de l'action des diastases*, Paris, 1903.

CHAPTER X

Systems not in equilibrium—Treatment from the kinetic standpoint.—

Heterogeneous systems: Nernst's theory of heterogeneous reaction velocity—Heterogeneous catalysis.

KINETICS IN HETEROGENEOUS SYSTEMS.

THE simplest conceivable type of heterogeneous reaction is the distillation of a pure liquid into a vacuum. If the vapour is withdrawn by some means, the rate of the production of the vapour by the liquid will be independent of time. It will likewise be independent of the mass of liquid present as long as any liquid remains. The reaction equation would be—

$$\frac{dx}{dt} = k, \text{ or } x_1 - x_2 = kt.$$

A similar state of things exists in the formation of many radioactive products, such as niton from a radium salt. Further examples of heterogeneous velocities of a more complex nature are met with in the rate of dissolution of solids in liquids, *e.g.* benzoic acid in contact with water, or marble in contact with hydrochloric acid. In the process of dissolution of a solid, we know that at length a point is reached beyond which no more solid will dissolve, or rather at this concentration, which is simply the solubility of the solid, the rate of solution is just equal to the rate of precipitation, a heterogeneous equilibrium being established. The study of the phenomena involved in the dissolution of a solid in a liquid with, or without, "chemical action," in the usual sense of the term, must be considered more closely. In the first place, it is evident that diffusion must play an important rôle. The fundamental expression for the diffusion of a substance already referred to in the preceding chapter was

given by Fick (*Phil. Mag.*, [4] 10, 30, 1855, being an excerpt from *Pogg. Ann.*, 94, 59) in the form of a differential equation, based on Fourier's expression for heat conductance, viz.—

$$\frac{\partial y}{\partial t} = -D \frac{\partial^2 y}{\partial l^2}$$

where y denotes concentration of the diffusing substance, t denotes time, and l denotes distance. D is the coefficient of diffusion, and may be defined as the quantity of substance, which during unit time will pass through unit sectional area from one stratum to the next adjacent one, the concentration gradient $\left(\frac{dy}{dl}\right)$ being unity.

The first investigation of importance on the subject of the velocity of dissolution of a solid in a liquid was undertaken by A. A. Noyes and W. R. Whitney (*Zeitsch. physik. Chem.*, 23, 689, 1897), who carried out measurements with benzoic acid and lead chloride, compressed into the form of small cylinders, which were rotated rapidly in water, the cylinder being removed from time to time, and the solute content in the aqueous solution determined analytically. The hypothesis which Noyes and Whitney formed, and which is fully borne out by their results, is that the solid substance is always surrounded by a very thin layer of saturated solution, and that the rate of dissolution is entirely dependent on the rate of diffusion of the solute from this saturated layer into the surrounding medium. This means that the *actual* dissolution of the solid is an extremely rapid process in comparison with the diffusion process, and it is the slower diffusion which determines the observed, *i.e.* the apparent, rate of dissolution of the solid. If S is the solubility of the solid, *i.e.* the concentration in the saturated layer, and x the concentration of the solute in the bulk of the solution at the time t , then the equation for the rate of dissolution is—

$$\frac{dx}{dt} = k(S - x)$$

assuming that the rate of diffusion, from one point to another,

is proportional to the difference of the concentrations at these points. On integration this equation becomes—

$$\frac{1}{t} \log \frac{S}{S-x} = k$$

where k is the dissolution constant. It will be observed that this expression is similar in form to a monomolecular chemical reaction. This does not mean that the actual dissolution process proceeds according to the monomolecular law, but that the total apparent dissolution being determined by a diffusion process, one necessarily obtains an expression of the above type. As Nernst pointed out later (*Zeitsch. physik. Chem.*, 47, 52, 1904), it is useless to attempt to settle the order of a heterogeneous reaction, such as that of marble dissolving in an acid solution, for the process which governs the reaction is the relatively slow diffusion, which will always cause the apparent dissolution velocity k to conform to a monomolecular type.

Some of Noyes' and Whitney's results are as follows :—

DISSOLUTION VELOCITY OF BENZOIC ACID INTO WATER.

t (minutes).	x (average value).	k .
10	6.35	112.1
30	14.78	109.1
60	21.60	107.5
	$S = 27.92$	
10	8.74	163
30	18.49	157.1
60	24.79	160.1

Analogous results were obtained with lead chloride. It will be observed that for each series, with different specimens of solid, the values for k are reasonably constant, and hence the hypothesis with regard to the layer of saturation is confirmed. It will be noticed, however, that the absolute values in the different series are by no means the same. k must, therefore be a composite quantity depending on the actual

physical condition of the surface of separate portions of the solid, *i.e.* the surface area, and also, as was shown later, on the rate of rotation of the solid, because this affects the saturated layer.

The effect of the area exposed to the solution was more carefully investigated by L. Bruner and St. Tolloczko (*Zeitsch. physik. Chem.*, **35**, 283, 1900), who used very smooth surfaces, and measured the area before commencing, so that the dissolution velocity constant could be referred to unit area, *i.e.*—

$$\frac{dx}{dt} = kO(a - x)$$

and regarding O as constant throughout the expression, one obtains—

$$k = \frac{1}{Ot} \log \frac{S}{S - x}$$

Experiments were carried out at a constant stirring rate with benzoic acid, phenyl-acetic acid, phenyl-propionic acid, acetanilide, and gypsum. The following data were obtained for benzoic acid in contact with water. Temperature 25°C ., S equivalent to 12.86 c.c. of a given baryta solution, $O = 26.8\text{ cm}^2$.

t hours.	x .	k .
0.25	0.87	0.00454
0.50	1.60	0.00431
0.75	2.32	0.00431
1.0	2.91	0.00417
1.5	4.30	0.00439
2.0	5.30	0.00431
2.5	6.20	0.00427
3.0	7.25	0.00448
3.25	7.52	0.00438
5.5	10.23	0.00471
		Mean = 0.00439

The constancy is satisfactory. Bruner and Tolloczko also carried out measurements on benzoic acid and on gypsum at 35°C . For benzoic acid dissolution $k_{35}^{\circ} = 0.0080$. Hence,

for 10° rise the velocity has a temperature coefficient of 1.8 in the case of benzoic acid. In the case of gypsum $k_{25} = 0.00233$, $k_{35} = 0.00351$. Coefficient per 10° rise = 1.5. It will be observed that the coefficient for these heterogeneous reactions is smaller than the coefficient of a monomolecular reaction in a homogeneous system (usually 2-3 per 10° rise). Bruner and Tolloczko noticed that in many of their experiments the surface of the solid was eroded. This would mean that the microscopic surface, as they call it, must be considerably greater at the end of the experiment than at the beginning. Yet a good constant has been obtained on the assumption that O remained constant. This can only be explained, as Bruner and Tolloczko point out, by assuming that there is a layer of saturated solution close to the solid, and the actual diffusion process really starts from the outer side of this layer, the "quadratic area of interface." Noyes' and Whitney's assumption is therefore strongly supported by Bruner's and Tolloczko's observations.

In the *Zeitsch. physik. Chem.*, 47, 52, 1904, Nernst put forward a general theory of heterogeneous reaction velocity, which was experimentally confirmed by E. Brunner (*Zeitsch. physik. Chem.*, 47, 56, 1904), and by the later work of others. According to this theory, the actual chemical reaction between, say, a solid such as marble and an aqueous solution of hydrochloric acid, is very rapid compared to the rate of diffusion of the hydrochloric acid, from the bulk of the solution into the Noyes-Whitney layer. According to Nernst, if O is the "effective" surface area of the solid, *i.e.* outer area of the layer in contact with a solution whose volume is V , and δ the thickness of the layer, and if D is the diffusion coefficient of the diffusing substance, namely, hydrochloric acid, per unit area per second per unit concentration difference, then in time dt the quantity dx , or—

$$\frac{OD(a-x)}{V\delta} dt$$

of hydrochloric acid will diffuse into the layer. V comes into the expression in order to make $\frac{a-x}{V}$ a concentration term,

which denotes the actual concentration of hydrochloric acid in the bulk of the solution at the time t . But applying an equation of the Noyes-Whitney type to this process, we obtain—

$$dx = k(a - x)dt$$

and hence k , the dissolution velocity, may be expressed—

$$k = \frac{OD}{V\delta}$$

The greater the surface area, the greater will k be, the faster the rotation of the solid, the smaller will δ become, and hence the greater will k be. For the rate of dissolution of benzoic acid in water, we can therefore write—

$$\frac{dx}{dt} = k(S - x) = \frac{OD}{V\delta} (S - x)$$

From the observed value of k , and the observed values of V , O , and D , we can calculate δ , the thickness of the layer, for a given rate of stirring.¹ Brunner calculated this as follows:—

TEMPERATURE = 20° C.

Reaction.	k (for stirring rate of 150 revolutions per minute).	D .	δ (for stirring rate of 150 per minute).
Benzoic acid (fused) in water	2.3	0.75	(20 μ) = 0.020 mm.
Magnesia in benzoic acid .	1.55	0.75	0.029 "
Magnesia in acetic acid . .	2.05	0.95	0.028 "
Magnesia in hydrochloric acid and magnesium chloride .	8.1	6.7	0.050 "
Marble in hydrochloric acid and magnesium chloride .	11.0	6.7	0.036 "
Magnesium in benzoic acid .	2.1	0.75	0.0215 "
Silver acetate in water . .	1.55	1.0-0.8	0.039-0.031 "
Electrolysis of benzoic acid .	1.45	0.75	0.031 "

The values of δ are of the same order throughout, thereby

¹ Brunner found that the dissolution rate (k) was $\propto \frac{2}{3}$ power of the rotation frequency.

pointing to the physical nature of the velocity process. The above data on the rate of solution of magnesia in benzoic and acetic acids show further that it is not the strength of the acid (benzoic is stronger than acetic), but their diffusion rates which determine the reaction velocity; for acetic acid reacts more rapidly than benzoic acid owing to its greater diffusion.

In the illustrations which have been given the characteristic common to all is that the chemical reaction velocity is very great compared to the diffusion rate. An exception to this occurs in the hydrolysis of esters suspended in water (H. Goldschmidt, *Zeitsch. physik. Chem.*, **31**, 235, 1899). With regard to criticism of the diffusion theory of heterogeneous reaction velocities, one may perhaps mention that of Meyer Wildermann (*Zeitsch. physik. Chem.*, **66**, 445, 1909), which is, however, of doubtful value.

As already pointed out, if the heterogeneous velocity is really that of a diffusion process, one will always get a monomolecular constant independent of the actual order of the more rapid chemical reaction, which accompanies the diffusion process. By way of recapitulation, the following characteristics of heterogeneous reaction may be noted—

(1) The connection between the reaction constant and the diffusion constant is given by—

$$k = \frac{OD}{\delta V}$$

and this must be verified by the data.

(2) Whatever influences the viscosity of the solution must necessarily alter D , and hence alter k .

(3) The rate of rotation of the body (or of the liquid surrounding the given body) must likewise alter the velocity constant.

(4) The temperature coefficient of k must be of the order of 1.28 for 10° rise (Trautz and Wedekind have found cases of *homogeneous* reaction velocities with very small temperature coefficients).

[“On the factors which determine crystal habit,” see R. Marc and A. Ritzel, *Zeitsch. physik. Chem.*, **76**, 584, 1911,

who deal with the problem from a thermodynamic standpoint].

Certain Radioactive Changes.—Radioactive changes are practically always heterogeneous, so that the physical state of the resultant is usually different from that of the reactant, *i.e.* a gas gives rise to a solid, or a solid gives rise to another solid, with which it is presumably immiscible. They have not been investigated from the standpoint of the diffusion law and have therefore been introduced as illustrative examples, into the section dealing with *homogeneous* reactions. The problem of the rate of absorption of α or β rays by different media is, however, evidently a diffusion process, and attention may be briefly drawn to one or two cases. The Noyes-Whitney expression as such, has not been applied. Instead, the monomolecular reaction expression, which we have seen is identical in form with the diffusion expression, has been employed and has been found to correspond to these processes very closely. Thus, in the case of α rays from radium¹ or polonium, the active preparation was covered with successive layers of aluminium foil the ionisation produced in the air chamber above the foil being determined in the usual way by the rate of leakage from a charged electroscope. By this means it was found that the ionization depended on the thickness of the aluminium layer according to the usual exponential or "compound interest" law, *i.e.* if I is the intensity of ionisation (which of course is a direct measure of the number of α particles) when the aluminium foil thickness is r , and I_0 is the intensity when there is no aluminium foil, then the following expression holds:—

$$I = I_0 e^{-kr}$$

This may be written—

$$\frac{1}{r} \log \frac{I_0}{I} = k$$

which is the more usual chemical form. This law is true as long as the thickness of the aluminium does not exceed a certain value. When this value is exceeded the ionisation in the chamber above falls much more rapidly, this evidently

¹ Rutherford and Miss Brooks, *Phil. Mag.*, July, 1902.

being due to the fact that the α rays are no longer getting through this thickness of foil. This gives the "range" of the α particles in aluminium. In addition to liquids and gases, metals are known to absorb the α rays, and the extremely simple and general rule is that the absorption is directly proportional to the density of the absorbing medium, and does not depend on its chemical constitution. This holds even when we compare two substances so dissimilar as air and aluminium. What has been said of α particles holds equally well for β rays, though these rays are of course much more penetrating. The density law holds in all cases with the exception of lead and tin.

HETEROGENEOUS CATALYSIS.

It has long been known that a reaction which goes on extremely slowly by itself may be greatly accelerated if a piece of platinum or other substance is introduced into the system. Two important instances of the technical application of such heterogeneous catalysts are the "contact process" of sulphuric acid manufacture, and the preparation of chlorine by the passage of hydrochloric acid and oxygen over pumice impregnated with a copper salt, *e.g.* cupric chloride in the "Deacon Process." To systematise our considerations we may divide heterogeneous catalysis into two groups—

(1) Catalysis of a gaseous reaction by the introduction of a solid.

(2) Catalysis of a reaction occurring in solution, by means of a solid or a colloidal substance.

1. *Heterogeneous Catalysis in Gaseous Systems.*—Our information on this subject we owe chiefly to Bodenstein and his co-workers (*Zeitsch. physik. Chem.*, 1903, 1904, 1905, 1907). The most important case is that already mentioned, *viz.* the contact process of sulphuric acid manufacture. In this, sulphur dioxide and oxygen are made to combine at a fairly high temperature, the catalyst being platinum, in the form of sponge, wire, etc. The stoichiometric equation is—



i.e. if this were also the reaction velocity expression, one would get a *termolecular* constant. Bodenstein found that this was

not the case (an illustration of its inapplicability will be given later). The expression which was found to be most applicable was a modified monomolecular one, that is a monomolecular expression upon which was superimposed a term for the quantity of sulphur trioxide formed, and which was found to retard the progress of the reaction, so that Bodenstein's expression is similar in form to that of a negative catalysis, which we have already studied. The expression for the rate of the reaction is as follows :—

$$\frac{dx}{dt} = \frac{k(a-x)}{x^{\frac{1}{2}}}$$

where $(a-x)$ represents the amount of sulphur dioxide at a given moment, and x is the amount of sulphur trioxide at the same time. This expression is quite different from that which one would expect from a reaction in a homogeneous system, *i.e.* a reaction which could go on in the absence of a solid catalyst. The above expression on integration becomes—

$$k = \frac{1}{t} \left(a^{\frac{1}{2}} \log \frac{a^{\frac{1}{2}} + x^{\frac{1}{2}}}{a^{\frac{1}{2}} - x^{\frac{1}{2}}} - 2x^{\frac{1}{2}} \right)$$

(It becomes a little more complicated if one allows for the addition of some sulphur trioxide at the beginning, *cf. Zeitsch. physik. Chem.*, 60, 13, 1907.)

The following data are taken from a typical experiment by Bodenstein :—

k is calculated as above. Temperature = 248° C.

"a" (SO₂) = 370.4 mm. mercury.

t (min.).	5.	10.	15.	20.	30.	40.	50.
x . .	64.3	97.0	120.9	141.1	174.9	198.8	223.5
k . .	0.208	0.205	0.201	0.199	0.199	0.194	0.200
t (min.).	60.	70.	80.	90.	100.	120.	150.
x . .	241.0	255.2	269.5	281.2	292.1	309.7	329.2
k . .	0.199	0.196	0.199	0.200	0.202	0.205	0.209

Mean k = 0.201.

In the above case the quantities of sulphur dioxide and oxygen were chosen initially equivalent. Bodenstein showed that on employing excess oxygen no effect was introduced— k was still constant throughout any series of determinations, and its value was very close to that obtained from the equivalent mixtures at the same temperature. With sulphur dioxide in excess, however, the constant was no longer good, and its absolute value was considerably lower than in the case in which the two gases are present in equivalent quantities. To account for this remarkable behaviour of a reaction which one would naturally have supposed to be termolecular, Bodenstein assumes that the velocity of combination of sulphur dioxide and oxygen, at the surface of the platinum is extremely rapid, and that the velocity of the reaction actually measured is that of the diffusion of sulphur dioxide up to the surface of the platinum, this diffusion being hindered by the accumulating quantity of sulphur trioxide which is formed at the platinum surface, and through a layer of which the sulphur dioxide has to pass. This assumption would lead us to expect an apparently monomolecular effect modified by a negative catalysis term involving the sulphur trioxide concentration. That the sulphur trioxide term appears as an exponential ($\frac{1}{2}$) will be rendered intelligible when we remember that the layer of sulphur trioxide, must be of the nature of an adsorption layer, the surface concentration being generally (concentration in bulk)ⁿ. Bodenstein applied his equation to the data of earlier experimenters, notably, those of Bodländer and von Köppen, with the following results. k_3 is added for comparison, it denotes the "constant" of a *termolecular* reaction. It will be observed that the values of k are extremely constant. It is not, however, clear why the anticatalysis term $[\text{SO}_3]^{\frac{1}{2}}$ should appear in the denominator; one would have as readily expected to find it as a separate quantity with a negative sign.

t (hours).	$x(\text{SO}_3)$.	$k_2 \times 10^{10}$.	k (Bodenstein), Temp. = 182°C .
0.5	12	183	0.0043
1.0	20	161	0.0046
1.5	27	153	0.0049
2.0	32	140	0.0049
2.5	36	131	0.0047
3.0	40	117	0.0046
3.5	43.5	119	0.0046
4.0	46.5	115	0.0044
5.0	52	108	0.0043
6.0	57	103	0.0041
7.0	62	101	0.0041
8.0	67	101	0.0041
9.0	72	101	0.0041
10.0	76	100	0.0041
11.0	80	100	0.0041
12.0	84	100	0.0041

In Bodenstein's words (*l.c.*, p. 61) "a full explanation of all the phenomena (of heterogeneous catalysis of gas reactions) is given by the assumption that the reaction process is retarded by the product of the reaction in those cases in which this product is more easily condensable and more easily absorbed, than the initial reactants themselves. There is in fact an adsorption layer, or in certain cases an ordinary liquid or solid skin formed upon the catalyst, through which the reactants must pass by diffusion in order to come into contact with the catalyst, where they react with practically instantaneous velocity."

For further details Bodenstein's papers must be consulted. A natural inference drawn by Bodenstein, from the results obtained in heterogeneous catalysis of gaseous reactions in general, is that the walls of the vessel which contains the gas mixture must also act in a similar manner, for Bodenstein's theory of catalysis is essentially a physical one, and catalytic properties ought to be possessed by every kind of surface. He showed this to be actually the case, thereby explaining certain anomalies which had been noted by previous experimenters. No gaseous reaction therefore is entirely uncatalysed, for the containing vessel must also exert an effect, though by

suitable arrangement this may be made extremely small. Practically the first instance in which this phenomenon was carefully examined was when van 't Hoff (*Etudes*, 55, 1884) showed that the rate of polymerisation of cyanic acid depended upon the superficial area of the walls of the vessel. On heating the same quantity of cyanic acid in a simple bulb and in a spiral respectively, it was found that the rate of polymerisation was much greater in the latter case.

2. *Heterogeneous Catalysis in Liquid Systems.*—The catalytic agents in such cases are solids like platinum sponge, or colloidal particles such as are found in colloidal platinum solution or enzymes, which very closely resemble colloidal particles. To show the similarity in action between a colloidal solution of platinum and a blood enzyme (blood katalase), one may quote the respective data obtained by Bredig and Senter for the decomposition of hydrogen peroxide in aqueous solution by their means.

Blood Katalase (Senter).			Colloidal platinum (Bredig and Muller von Berneck).		
t (mins.).	$C_{H_2O_2}$.	k (monomolecular).	t .	$C_{H_2O_2}$.	k (monomolecular).
0	39.7	—	0	47.4	—
5	32.2	0.0175	10	37.9	0.0097
10	26.7	0.0163	20	30.0	0.0099
20	17.8	0.0176	30	23.6	0.0101
30	11.6	0.0185	40	18.2	0.0104
50	4.8	0.0191	60	11.0	0.0106

Note that the reaction is monomolecular (or apparently monomolecular in both cases). Owing to the similarity in behaviour between colloidal metal solutions and enzymes, Bredig has called the former inorganic ferments (*cf.* Bredig's monograph, *Anorganische Fermente*). Bredig (with Teletow), *Zeit. Elektrochemie*, 12, 581, 1906, has also shown in the case of the catalytic decomposition of hydrogen peroxide in aqueous solution by means of a cylinder of platinum foil rotated at a constant rate, that the reaction velocity constant is a monomolecular one, but that it differs from the ordinary monomolecular constant in homogeneous systems in that the

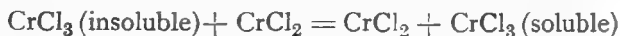
numerical value of the constant is inversely as the volume of the solution. A few of Bredig's results are—

Constant rotation frequency (245 revs. per minute).

Volume in c.c.	$0.4343k$ at 25°C .
450	0.0060
675	0.0046
1350	0.0020

It is found in fact that kV is constant.

Bredig and Teletow also verified Bruner's conclusion as regards the "quadratic dimensions" of the foil being the effective surface, which we have already seen is due to the thin saturated layer being the actual surface of reaction. An excellent account of heterogeneous catalysis is given by Bredig in his Vortrag (already alluded to in the preceding chapter). For our present purpose a very useful summary of the theories of heterogeneous catalysis is given by Denham (*Heidelberg Dissertation*, 1909, *Zeitsch. physik. Chem.*, **72**, 641, 1910), which will be fairly closely followed here. First let us take some typical instances of heterogeneous catalysis. A familiar illustration in organic chemistry is the effect of aluminium chloride such as in Friedel-Craft's method of synthesising aromatic hydrocarbons. Also the effect of catalytic agents on the rate of dissolution of solids is very clearly shown by violet chromic chloride (insoluble), which only dissolves very slowly in water, but may be made to do so very quickly if a minute trace of chromous chloride is present. (It is assumed that the reaction here is—



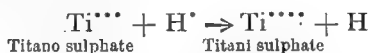
the newly formed chromous chloride again reacting with further quantity of insoluble chromic salt.)

The dissolution of impure zinc (*i.e.* containing traces of iron) in hydrochloric acid might also be looked upon as heterogeneous catalysis. The actual mechanism in this process is fairly well understood, *viz.* the production of short circuits between pieces of iron and zinc, and the consequent electrolysis

and dissolution of zinc, which has a much greater solution pressure than the iron. The most frequently investigated case is the decomposition of hydrogen peroxide, which always takes place according to a unimolecular law. Hydrogen peroxide solutions can be decomposed with the evolution of oxygen, by colloidal platinum, and by spongy and solid platinum. Teletow (Bredig and Teletow, *Zeitsch. Elektrochemie*, **12**, 581, 1906), has shown also that in the latter case the decomposition of hydrogen peroxide follows the Nernst diffusion theory, first in that it is apparently monomolecular, secondly, in that the rate decreases when the solvent is made more viscous by the addition of sugar to the water, and, thirdly, by the fact, that the temperature coefficient is only 1.28 for 10° C. Platinised platinum has been found a very efficient catalyst for the oxidation or reduction of ions. Thus Oberer (*Diss.*, Zurich, 1903), observed an increase in the oxygen evolution from a solution of cobaltic sulphate (reduction taking place) on introducing a small piece of platinum wire, and Manchot and Herzog (*Ber. chem. Gesell.*, **33**, 1742, 1900) found that platinum exerted an accelerating influence on the (oxidation) reaction—



Spencer and Abegg (*Zeitsch. anorg. Chem.*, **44**, 379, 1905) also showed that thalious ions could be transformed into thallic ions, under similar conditions as regards catalyst (oxygen gas being present at the same time). Diethelm and Förster (*Zeitsch. physik. Chem.*, **62**, 129, 1908), have also investigated the reaction—



which takes place in acid solution [*i.e.* H^{*} present] at a platinum cathode. The same reaction was comprehensively studied by Denham (*l.c.*), who employed a rapidly rotating platinum gauze cylinder as the catalyst, and who showed that the above reaction was strictly monomolecular (Denham, it may be remarked, used strongly acid solutions, H^{*} being thus constant). Denham also succeeded in observing the equilibrium which is reached in the above reaction by approaching

it from both sides (*i.e.* hydrogen gas is either absorbed or evolved according to circumstances). As regards the effect of temperature, Denham found a temperature coefficient of 1.29 for 10°, *i.e.* a very small one.¹ A heterogeneous catalyst hastens a reaction, and the greater the surface exposed, the greater is the reaction velocity. As a rule, however, the catalyst does not effect the equilibrium constant (when such is measurable). Such appears to be the case, as we find the catalyst at the end of the experiment in exactly the same amount, and in exactly the same chemical or physical state as at the commencement. Cases are known, however, to which the term "catalysis" is applied, in which the catalyst is itself altered. In such cases it has taken a permanent part in the reaction, and the equilibrium (if such is measurable), will have been correspondingly shifted.

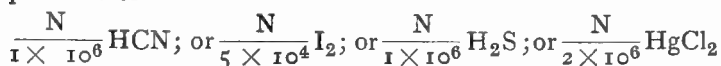
Having giving some typical instances of reactions catalysed heterogeneously, mention must be made of a characteristic peculiarity, namely, the poisoning of the catalyst. Many catalysts after some use lose their efficiency. This is particularly true of colloidal metal solutions and enzymes. Considering the familiar reaction, namely, the decomposition of aqueous solutions of hydrogen peroxide, it has been noticed that very small traces of hydrocyanic acid, iodine solution, mercuric chloride, destroy the activity of ferments, and Bredig found quite an analogous behaviour in the case of colloidal metals. Thus, in order to reduce the rate of decomposition of hydrogen peroxide, by a given solution of colloidal platinum² to *one-half* its normal value, it is only necessary to have the following substances present at the concentrations:—

HCN	5	× 10 ⁻⁸	normal
ICN	7	× 10 ⁻⁸	,,
I ₂	7	× 10 ⁻⁶	,,
HgCl ₂	2.5	× 10 ⁻⁶	,,

¹ Other interesting results obtained by Denham, such as the quantitative reduction of hydrocyanic acid to methylamine by hydrogen gas in presence of platinum gauze, cannot be referred to here at length.

² Containing $\frac{1}{10^5}$ atoms of platinum per liter.

Senter also found that, using blood katalase as the catalyst for the same reaction, the normal value was reduced to $\frac{1}{2}$ in presence of—

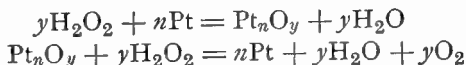


The striking similarity between colloidal solutions and enzymes is here clearly brought out.

Pulsating Catalysis.—Examples of *periodic* velocities are to be found, for example, in the dissolution of chromium in acids, and in the electrolytic passivity of iron. Bredig discovered a much more reproducible instance, namely, the pulsating catalytic decomposition of hydrogen peroxide at a mercury surface. Slight additions of salts, alkalies, or acids had a marked effect. The source of this remarkable phenomenon was found to be an explosive unstable peroxide of mercury HgO_2 , which has been isolated by von Antropoff (*Zeitsch. physik. Chem.*, 62, 513, 1908).

Theories of Heterogeneous Catalysis.—One may divide these theories into two classes, the chemical and the physical. The chemical view consists in supposing the existence of intermediate chemical compounds which are unstable; the physical view explains the phenomenon as due to the condensation or increase in concentration of the reactants at the surface of the catalyst—such increase in concentration being brought about by capillary forces.

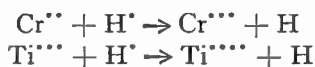
As an example of the chemical view one may quote the following from Bredig's *Anorganische Fermente*:—"Haber's view that platinum catalysis in the decomposition of hydrogen peroxide consists in an alternate oxidation and reduction of the metal according to the equations—



seems to me to be the best explanation of the phenomena at present known."

The only outstanding instance in which the active intermediate compound has been isolated is the peroxide of mercury,

HgO_2 , there is no evidence for the existence of an intermediate compound in the catalysis of the same reaction by platinum, either as solid metal or in the colloidal state. In fact, Wöhler, (*Ber.*, 39, 3538, 1906; 42, 3326, 1909) actually showed that PtO and PtO_2 were less catalytically active than platinum itself in the "contact process" (sulphur dioxide + oxygen), but that, as the reaction was continued, the activity of the catalyst was increased, and analysis showed at the close of the reaction that the oxides had been completely reduced to metal. It is still more difficult to conceive that an oxide is the actually active catalyst in reactions where hydrogen gas is evolved, *i.e.*—



No proof, it may be mentioned, has been brought forward that a platinum hydrogen compound exists.

The physical theory—which we have already mentioned in connection with Bodenstein's work—may be said to have been put forward for the first time by Faraday (1834), who considered that the reactants (gases) were bodily absorbed by the metal. J. J. Thomson put forward a modified form of this, in that it is supposed that capillarity is the origin of the effect which is thus a surface phenomenon. This view has received more support than any other.

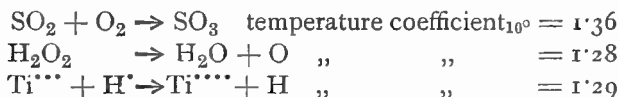
Gibb's fundamental expression for adsorption (see Part II. Vol. II., Chap. X.) is—

$$\Gamma = \frac{-C}{RT} \cdot \frac{d\sigma}{dc}$$

If δ is the thickness of the adsorbed layer, then the concentration in the layer is $\frac{\Gamma}{\delta}$, and this is the term for the active mass of the solute—supposing we are dealing with a liquid solution—at the surface of the catalyst. This concentration term is much greater than that in the bulk of the solution, and hence the reaction goes more quickly when the solid is present—the actual velocity, we assumed, being the rate of diffusion of the reactants through the resultants. Let us

examine some of the characteristics of certain heterogeneously catalysed reactions and see how the adsorption theory fits the facts. Bredig and Müller von Berneck found that the catalytic decomposition of hydrogen peroxide by colloidal platinum was not strictly monomolecular, as the constant rose when the hydrogen peroxide concentration was small. Freundlich (*Kapillarchemie*, p. 382) ascribes this to adsorption, as the experimental (empiric) adsorption formula $x = kc^{\frac{1}{n}}$ shows the concentration (x) in the surface layer does not fall so quickly as that of the bulk of the solution (c), so that since Bredig and von Berneck calculated their constant from bulk concentration values, one would expect a rise towards the end of the experiment, as there is not quite direct proportionality between bulk and surface values.

The next point is temperature coefficient. In reactions which are catalysed either by colloidal metals, etc., or by enzymes, the coefficient for a 10° C. rise is at least 2 (*i.e.* the same order as we find for an uncatalysed reaction going on in a homogeneous system). In the cases where solid catalysts are employed, however (such as platinum gauze), the temperature coefficient is much less, being only about 1.3. The following are some examples:—



There is, therefore, a characteristic difference between the behaviour of colloidal (or enzyme) and solid catalysts. This problem might be considered as follows: As often pointed out, it is the slowest of a series of processes, which determines the total rate of the reaction. Now adsorption is known to be an exceedingly rapid process. If now the reacting substances were brought to the surface of the catalyst by capillary forces, the temperature coefficient would correspond to that of the slower process, *viz.* the chemical process in this case. If, on the other hand, the reacting substances are brought to the surface by the slow process

of diffusion, for the range of molecular capillary attraction is very small, then the measured velocity would be that of a diffusion process, and the temperature coefficient would be of the low order of 1.5, which we have seen is the case when solid catalysts are used. To account for the high velocity coefficient in colloid or enzyme catalysis, we might consider that the Brownian movement of these particles acted as very efficient stirring—so efficient, in fact, that the diffusion layer was removed as fast as it was formed, with the result that the (homogeneous) chemical action in the adsorbed layer is the real process whose coefficient we measure. One would expect on this view a high temperature coefficient. But does the Brownian movement remove the diffusion layer? Bredig and Teletow (*Zeitsch. Elektrochemie*, 12, 583, 1906) have calculated the thickness of the layer from the Nernst diffusion

expression, viz. $K = \frac{OD}{\delta V}$, from the data given by the hydrogen

peroxide decomposition in the presence of colloidal platinum, and found that $\delta = 0.05$ mm., *i.e.* of the same order as Brunner found in the case of the dissolution of benzoic acid in water. This seems to show that in spite of the Brownian movement the diffusion layer remains unchanged. If this is so, then the above explanation of the high temperature coefficient in the case of colloids and enzymes breaks down. (Unless we indeed assume with Senter that the whole surface of the colloid is not effective, but the effective area increases with temperature rise (Bredig and Teletow assumed it was entirely effective), Senter's reason being the extraordinary sensitivity of colloids to a mere trace of "poison," *e.g.* (HCN).) The point is not, therefore, settled. Another attempt at an explanation of the difference in behaviour as regards temperature coefficient is suggested by Denham, as being connected with the fact that the surface energy of a small particle is greater per unit area than the energy of a solid or plane surface, *i.e.* small crystals are more soluble than large ones. Hence the adsorption effects at a colloid particle surface are greater than those at a plane surface such as platinum gauze of the same area; but even if this is so, diffusion, one would

think, should be the slowest process present. Capillary forces are only effective over an extremely short range, and though the adsorption is rapid (practically instantaneous) when solute is in the neighbourhood of the surface, the process whereby the depletion of solute is made good must be a diffusion one, and whether the surface energy is high or low seems to have very little to do with it. Looking at the question as a whole, it strikes one as most probable that the difference in temperature coefficient between colloid catalysis and solid catalysis is really due to the Brownian movement possessed by the one type of catalyst, and not possessed by the other. The fact that the thickness of the layer calculated by Bredig and Teletow is of the order of that in the benzoic acid case, may after all be accidental (as would be the case on Senter's view), though there is no evidence either way. The ultimate explanation of the difference in the behaviour of colloids and enzymes as distinct from solids, in regard to temperature coefficient of one and the same reaction, is yet to be found.

Some interesting results obtained by Armstrong (*Proc. Roy. Soc.*, 73, 508, 1904) on the subject of enzyme (lactase) action upon milk-sugar hydrolysis, must be mentioned in connection with heterogeneous catalysis, and especially from the standpoint of the adsorption or physical theory of the same. Armstrong showed that when concentrated milk-sugar solution is hydrolysed with small quantities of lactase, the hydrolysed mass, at a given time (46 hours), even in solutions of very different concentration, was *the same* and in no way proportional to the sugar concentrations, as the Law of Mass Action would lead one to expect. He found—

Initial concentration of milk sugar.	Per cent. hydrolysed in 46 hours.	Absolute mass of sugar hydrolysed.
10 per cent.	22.2	2.22
20 ,,	10.9	2.18
30 ,,	7.7	2.21

In dilute solution, on the other hand, in which the enzyme

was present in large amount compared to the amount of sugar, Armstrong found that the percentage hydrolysed was strictly proportional to the sugar concentration :—

Initial concentration of milk sugar in 100 c.c. solution.	After 3 hours, quantity of sugar hydrolysed.	Velocity constant (monomolecular).
1.0 gram.	0.185 gram.	0.0296
0.5 ,,	0.098 ,,	0.0298
0.2 ,,	0.0416 ,,	0.0337

It was shown by the writer (*Phil. Mag.*, April, 1909) that a 6 per cent. *cane*-sugar solution has a small effect upon the interfacial tension, oil/water, and Freundlich has shown in agreement with this, that bodies containing hydroxyl are positively adsorbed (though not strongly). This means that in sugar solutions at high bulk concentration a state at the surface is reached which corresponds to surface saturation, the surface concentration remaining practically the same even when the bulk concentration is largely increased. The quantity of sugar hydrolysed in Armstrong's experiments depends on the adsorbed quantity, and, as we have seen, this is practically independent of the bulk concentration changes (when there is considerable sugar present), and hence one can see, on the adsorption theory, a very plausible basis for the rather remarkable observations made in the case of strong solutions of milk sugar in presence of a given limited amount of enzyme. Hudson (*Jour. Amer. Chem. Soc.*, 30, 1160, 1564, 1908) obtained similar results in the hydrolysis of cane sugar with invertase. If this view is the correct one, the greater the adsorption capacity of the substance the more marked will be the divergence from the mass action principle, *i.e.* the rate of decomposition should be $\frac{dx}{dt} = k$ over a considerable range of *bulk* concentration. It is assumed here that, owing to Brownian movement, the diffusion part of the process is masked.

INDEX TO SUBJECTS

A

- α rays, 67 *seq.*
 Abnormal substances. *See* Polymerised substances.
 Absorption spectra of solutions, 243, 244
 Acetic acid, molecular weight, 127
 "Active mass," 133, 134
 Addition of excess of one of the reacting constituents on equilibrium, effect of, 170 *seq.*
 Addition of inert gas on equilibrium, effect of, 168 *seq.*
 Adsorption, 418, 506 *seq.*
 Amphoteric electrolytes, 318-324
 Analytical chemistry, principles of, 380 *seq.*
 Anomaly of strong electrolytes, 267 *seq.*
 Association, molecular, in liquids, 124 *seq.*, 214
 Atom, inertia of an, 64
 —, structure of the, 59, 62 *seq.*
 Atoms, constitution of, 40 *seq.*, 44
 Attraction, molecular, 10, 94 *seq.*
 Autocatalysis, 457, 473 *seq.*
 "Avogadro Constant," *i.e.* the number of molecules in one gram-molecule, 22 *seq.*, 30 *seq.*, 38
 Avogadro's hypothesis, 6, 7, 202 *seq.*, 232 *seq.*

B

- β rays, 67 *seq.*
 Behaviour of gases and liquids, 72 *seq.*
 Bimolecular reactions, 437 *seq.*
 Boiling point Law of Ramsay and Young, 120
 — — of solution, rise of, 240
 Boyle's Law, deduction of, 5 *seq.*, 39, 73 *seq.*, 195 *seq.*
 Brownian movement, 508 *seq.*
 — — and molecular reality, 21 *seq.*, 31, 57
 — — in gaseous medium, 56

C

- γ rays, 67 *seq.*
 Caillietet-Mathias Law, 85, 86
 Calorie, 74
 Cane sugar, inversion of, 130 *seq.*, 245, 246, 284, 299, 301, 435, 436, 465 *seq.*, 510
 Caoutchouc, 416
 Catalysis, homogeneous, 130, 131, 244-246, 284, 299-301, 324-328, 435 *seq.*, 466 *seq.*
 — in heterogeneous systems, 149, 159, 164, 497 *seq.*
 — in mixed solvents, 479 *seq.*
 —, pulsating, 505

Catalysis, theories of heterogeneous, 505 *seq.*
 Cataphoresis, 257, 402
 Characteristic equations, 81, 90 *seq.*
 Charge on electron. *See* Electron.
 Chemistry of the radio-elements, 68
 Chlorine manufacture, 159 *seq.*
 Clausius equation, 111 *seq.*
 Cohesion, 94, 95, 102, 113 *seq.*
 Colloidal particles, Brownian movement of, 401 *seq.*
 — — —, coagulation of, 409 *seq.*, 417 *seq.*
 — — —, diffusion of, 398 *seq.*
 — — —, electrical charge on, 402 *seq.*, 413 *seq.*
 — — —, in precipitates, 412, 413
 — — —, molecular weight of, 398
 — — —, optical properties of, 399
 — — —, osmotic pressure of, 398 *seq.*
 — — —, protective effect of, 412
 — — —, size of, 399 *seq.*
 Colloidal solutions. Chap. VIII.
 — — —, stability of, 419, 420
 — — — viscosity of, 416 *seq.*
 Complex ions, 247, 269
 Compressibility of colloidal solutions, 39
 — — — of gases, 95
 Condensation of vapour upon electrically charged particle, 48
 Conductivity, electrical, of metals, 58
 — — — of solutions, electrical. *See* Electrolysis and Electrical resistance.
 — — —, thermal, of metals, 58
 Consecutive reactions, 447 *seq.*
 Constant, equilibrium. *See* Equilibrium.
 — — —, velocity. *See* Velocity.

“Contact” process of sulphuric acid manufacture, 164 *seq.*, 497 *seq.*
 Continuity of state, 72, 79 *seq.*, 87 *seq.*
 Corpuscles. *See* Electrons.
 Corresponding states, principle of, 108 *seq.*
 Critical constants, calculation of, 98, 116, 118
 — — — data, 80, 104, 105
 — — — pressure, 79 *seq.*, 85
 — — — temperature, 79 *seq.*, 85, 350
 — — — volume, 79 *seq.*, 86

D

Deacon process, 159 *seq.*, 176 *seq.*
 Decay, law of radioactive, 68
 Degrees of freedom (mechanical), 43
 — — — (Phase Rule). *See* Phase Rule.
 Density, abnormal gas, 153 *seq.*
 — — — of solutions, 240 *seq.*
 Depression of freezing point, molecular, 212 *seq.*, 240
 Diameter of molecules, 14 *seq.*, 19, 20
 Dibasic acids, electrolytic dissociation of, 266 *seq.*
 Dielectric constant of gases, 14
 Dieterici, equation of, 113 *seq.*
 Diffusion coefficient, 427, 428
 — — —, Einstein's theory of, 31 *seq.*
 — — — of electrolytes in solution, 421 *seq.*
 Dilute solutions, theory of, 194 *seq.*
 Dilution formula of van 't Hoff, 272
 — — — of Partington, 273
 — — — of Rudolphi, 271
 — — — Law of Ostwald, 262 *seq.*, 267 *seq.*, 333 *seq.*
 Disintegration of the atom, 67 *seq.*

Dissociating media, 127, 237 *seq.*,
330-339
— power, 127, 237 *seq.*
Dissociation constant, electrolytic,
262 *seq.*
—, electrolytic. *See* Electrolytic
Dissociation.
—, gaseous, 132, 150 *seq.*, 350,
363 *seq.*
— pressure, 132, 133, 350,
363 *seq.*
Distribution coefficient, 352
— Law of Nernst, 348 *seq.*,
352 *seq.*
— of base between acids, 284 *seq.*
— of molecules in space, 72 *seq.*
Double layer, electrical, 14, 402

E

Eighth order reaction velocity, 442
Einstein's theory of diffusion and
Brownian movement, 31 *seq.*
Electrical charge on an electrolytic
ion, 40, 47
— double layer, 14, 402
— resistance of solutions, measure-
ment of, 225 *seq.*
Electric field, effect upon a charged
particle, 45, 64
Electrocapillarity, 418, 419
Electrochemical equivalence, law
of, 224
Electrolysis, 223 *seq.*
Electrolyte, 215, 223 *seq.*, 257 *seq.*,
267 *seq.*
Electrolytes, diffusion of, 421 *seq.*
Electrolytic dissociation, 127, 213-
215, 217, 223 *seq.*, 257
seq., 330-339, 371
seq., 391 *seq.*
— —, degree of, 231 *seq.*, 257
seq., 391 *seq.*
— equilibria, heterogeneous, 371
seq.
Electromotive force, 251
T.P.C.—I.

Electron, charge on an, 47 *seq.*,
50 *seq.*, 52 *seq.*, 55
—, mass of an, 49, 64
—, ratio of charge to mass of
an, 58
— theory, 44 *seq.*
Electrons, rôle of, in metals, 57
—, sources of, 58
Emulsion particles, electric charge
on, 402, 403
— —, size of, 399 *seq.*, 415
Emulsions, 22 *seq.* Chap. VIII.
Endosmose, 257, 402
Entropy, 129
Eötvös-Ramsay-Shields method of
determining molecular associa-
tion, 125 *seq.*
Equation of state, reduced, 108 *seq.*
Equations of state, 81, 90 *seq.*
Equilibrium constant, 136 *seq.*, 147,
153 *seq.*, 157 *seq.*, 165 *seq.*,
184 *seq.*
— point, 130, 132, 133 *seq.*,
167 *seq.*, 262 *seq.*
Equipartition of energy, principle
of, 23 *seq.*, 44
Erg, 74
Esterification equilibrium, 185 *seq.*,
458 *seq.*
—, Goldschmidt's theory of,
482 *seq.*
Ethyl alcohol, molecular weight of,
127
Extraction, process of, 360 *seq.*

F

Fixation of nitrogen, 168
Franz-Wiedemann Law, 58
Freedom, degrees of (mechanical),
43
— — — (Phase Rule). *See*
Phase Rule.
Free energy, 129
Freezing point, depression of, 212
seq., 240

G

- Gas constant (R), 23, 73, 74, 202
 — law, 74 *seq.*, 202 *seq.*
 Gas-liquid heterogeneous equilibria,
 354 *seq.*
 Gas-solid heterogeneous equilibria,
 363 *seq.*
 Gaseous reactions. Chap. III.,
 p. 439
 Gases, molecular velocities in, 7, 8
 —, viscosity of, 8, 9
 Gay-Lussac's or Charles' Law, 6,
 198 *seq.*

H

- "Half-life period," 68
 Heat of dissociation, 250
 — of neutralisation, 248-250
 — theorem of Nernst, 121
 Helium atom, 67
 —, formation of, 71
 Heterogeneous catalysis, 497 *seq.*
 — equilibria involving ions,
 371 *seq.*
 — (chemical) equilibrium. Chap.
 VII.
 — reaction velocity. Chap. X.
 Homogeneous (chemical) equilib-
 rium. Chaps. III to VI.
 Hydrates in solution, 218-222
 Hydriodic acid decomposition, 140
seq., 169 *seq.*
 Hydrogen atom, mass of, 51
 — peroxide, decomposition of,
 501 *seq.*
 (Hydrol) monhydrol, dihydrol, tri-
 hydrol, 127
 Hydrolysis of salts, 289-304, 329,
 359 *seq.*, 388 *seq.*

I

- Ice, constitution of, 127

- Ideal solutions, 195
 Indicators, theory of, 304-316
 Inert gas upon equilibrium, effect
 of, 168 *seq.*
 Inertia of an atom, 63 *seq.*
 — of an electron, 64
 "Inorganic ferments," 501 *seq.*
 Internal pressure, 102, 103
 Iodine vapour, dissociation of, 156,
 175 *seq.*
 Ion alcoholates, 482 *seq.*
 — hydrates, 482 *seq.*
 Ionic product. *See* Solubility prod-
 uct.
 — — of water. *See* Water.
 — reactions and equilibria. *See*
 Electrolytic dissociation.
 — theory. *See* Electrolytic dis-
 sociation.
 Ionisation constant of water. *See*
 Water.
 — of a gas, 67
 Ions, 223 *seq.*
 —, diffusion of, 421 *seq.*
 Isochores, 91 *seq.*
 Isoelectric point, 413
 Isohydric solutions, 274-281
 Isolated reactions, 430 *seq.*
 Isothermals, 83, 88, 97, 106, 117
 Isotonic solutions, 196, 199, 201

J

- Joule, 74
 Joule's Law, 74

K

- Kinetic energy, 4 *seq.*
 — —, mean, of a molecule, 39

L

- Lactase upon milk sugar, action
 of, 509

Latex, rubber, 414 *seq.*
 Law of mass-action. *See* Mass-action.
 — of the rectilinear diameter, 85, 86
 Life period, average, 69
 — —, half, 68
 Liquefaction of gases, 79 *seq.*
 Liquid-liquid heterogeneous equilibria, 356 *seq.*
 Liquid systems, reactions in, 183 *seq.*, 218-222
 Liquids, molecular weight of, 125 *seq.*
 Lowering of vapour pressure, molecular, 206 *seq.*, 240

M

Magnetic field, effect of, upon charged particle, 45, 67 *seq.*
 Mass-action, law of, 131, 133 *seq.*, 187 *seq.*, 269 *seq.*, 284, 333, 509, 510
 Maxwell's theorem of distribution of velocities, 2 *seq.*
 Mean free path of molecules, 2, 8, 9
 Medium, catalytic effect of the, 476 *seq.*
 Membranes, semipermeable, 192
 Mercury, vapour pressure of, 122
 Metals, colloidal, 397 *seq.*
 Methyl alcohol, molecular weight, 127
 Migration of the ions, independent, 227 *seq.*
 Mixed acids, dissociation of, 282 *seq.*
 Mixtures, liquid, 184-192
 — of constant boiling point, 221
 "Mobile equilibrium," principle of, 136, 158, 187
 Mobility and diffusion, 423 *seq.*
 — of the ions, 227 *seq.*, 252 *seq.*, 255 *seq.*, 331, 334, 335

Molecular association, 124 *seq.*
 — attraction, range of, 10 *seq.*
 — diameter and radius, 14 *seq.*, 19, 20
 — surface energy, 125
 — velocities in gases, 7, 8
 — volume, 96
 — weight of liquids, 125 *seq.*
 — — of vapours, 125
 Molecules, constitution of, 40 *seq.*, 44
 —, real existence of, 20 *seq.*
 "Momentary" state, 171 *seq.*
 Monomolecular reactions, 431 *seq.*

N

Nebulium, 66
 Negative catalysis, 477 *seq.*
 Neon, formation of, 71
 Nernst's heat theorem, 121
 Neutralisation, heat of, 248-250
 Neutral salt action, 339
 Niton, 63
 Nitrogen, active, 170
 —, fixation of, 168
 — peroxide, dissociation of, 158, 159
 Non-aqueous solvents, electrochemistry of, 330-335
 Normal substances, 123 *seq.*

O

"Oil drop" method of determining charge on an electron, 52
 Opposing reactions. *See* Reversible reactions.
 Optical activity of solutions, 242
 — refractivity of solutions, 242
 Order of a reaction, 444 *seq.*
 Osmotic pressure, 192 *seq.*, 240
 — —, accurate measurement of, 204 *seq.*

P

- Partition coefficient. *See* Distribution coefficient.
 Periodic Law, 61
 Phase Rule, 348, 349, 351, 370
 Photo-electric effect, 58
 "Poisoning" the catalyst, 504, 505
 Polymerised substances, 105, 124 *seq.*, 238, 239, 353 *seq.*, 357 *seq.*
 Precipitate formation, 380 *seq.*
 Pressure, dissociation. *See* Dissociation.
 — exerted by a gas, 5
 —, internal, 102, 103
 — of saturated vapour. *See* Vapour.
 — on dissociation, effect of, 157
 —, osmotic, 192 *seq.*, 240
 Protyle, 63
 Pseudo-acids and pseudo-bases, 310, 317-318
 Pulsating catalysis, 505

Q

- Quadrimolecular reactions, 441
 Quinquemolecular reactions, 442

R

- Radioactive change, 67 *seq.*, 433 *seq.*, 455 *seq.*
 Radiometer, the, 20
 Radium Emanation (Niton), 63, 70, 434, 435
 Ramsay-Young boiling point law, 120
 — — —, equation, 90 *seq.*, 100
 Rate of reaction, 130 *seq.*, 429 *seq.*
 — — —, effect of pressure on, 466
 — — —, effect of temperature on, 461 *seq.*

- Reactants, 130
 Reactions, heterogeneous. Chap. X.
 — in gaseous systems. Chap. III.
 Recombination of gaseous ions, 439
 Rectilinear diameter, law of the, 85, 86
 Reduced equation of state, 108 *seq.*
 Refractive index of gases, 15
 — — of solutions, 242
 Resultants, 130
 Reversible reaction, 132, 447, 457 *seq.*
 Rotatory power. *See* Optical activity.

S

- Salt mixtures, dissociation in, 391 *seq.*
 Salts, hydrolysis of, 289-304, 388 *seq.*
 Saturated vapour, formulæ for pressure of, 120 *seq.*
 Side reactions, 447 *seq.*
 Simultaneous reactions, 447 *seq.*
 Solid-liquid heterogeneous equilibria, 370 *seq.*
 Solid-solid heterogeneous equilibria, 370
 Solubility product, 373, 375-394
 Solution, solid, 213, 341-347
 Solutions (liquid), 192 *seq.*
 — — —, diffusion in, 421 *seq.*
 — of electrolytes, 239-251
 —, theory of dilute, 194 *seq.*
 Solvation, 218-222, 332
 Specific gravity of solutions, 240 *seq.*
 — heat of gases, 41 *seq.*
 Stokes' Law, 28, 32, 48, 55
 Strength of acids, comparison of, 286 *seq.*
 Strong electrolytes, anomaly of, 267 *seq.*
 Sulphides, solubility of metallic, 385 *seq.*

Sulphuric acid manufacture, 164
 seq.
 — on alcohol, action of, 191
 Surface energy, molecular, 125
 — tension method of determining
 polymerisation in liquids, 125
 seq.
 Suspensions. Chap. VIII.
 —, electric charge on, 402

T

Tautomerism, 307 *seq.*, 317, 318
 Temperature coefficient of surface
 energy, 125
 —, definition of, from the kinetic
 standpoint, 4
 Tension, surface, 125
 Termolecular reactions, 439, 440
 Thermochemical comparison of
 strength of acids, 286, 287
 Thomson's, James, isothermals,
 87 *seq.*
 Transition from liquid to gas, 87
 Transmutation of the elements,
 67 *seq.*, 70, 71
 Transport number, 252 *seq.*

U

Unitary theory of electricity, 57
 Unpolymerised substances, 123 *seq.*

V

Van 't Hoff's theory of osmotic
 pressure, 194 *seq.*
 Vapour, constitution of water, 127
 —, molecular weight, 125, 369
 — pressure formulæ, 120 *seq.*
 — —, lowering of, 206 *seq.*
 — —, method of determina-
 tion, 122
 — — of ammonium chloride,
 369
 — — of mercury, 122
 Velocity constant, 131, 135 *seq.*
 — of ions, 252, 255
 — — —, measurement of
 absolute, 256 *seq.*
 Viscosity of gases, 8, 9
 — of liquids, 331, 332
 Volume method of comparing
 strengths of acids, 287 *seq.*

W

Waals, van der, equation, 94 *seq.*
 Water as a solute, 335-339
 —, constitution of liquid, 127
 — gas reaction, 174
 —, ionic product of, 290 *seq.*,
 324-330
 —, molecular weight in liquid
 form, 127
 — vapour, dissociation of, 154-
 156
 Wiedemann-Franz Law, 58

INDEX TO NAMES OF AUTHORS

A

Abegg, 226, 257, 268, 269, 280,
369, 389, 503
Aimée, 132
Amadori, 335
Amagat, 74 *seq.*, 81 *seq.*, 90, 127,
111
Andrews, 79 *seq.*, 87 *seq.*, 101
von Antropoff, 505
Appleyard, 389
Armstrong, 509, 510
Arndt, K., 335
Arrhenius, 210, 213, 214, 215, 217,
219, 225, 229, 231, 232 *seq.*,
276 *seq.*, 284 *seq.*, 288, 289, 297,
325, 330, 339, 390-392, 462 *seq.*
Auerbach, 386
Aulich, 352
Avogadro, 5, 6, 7, 193 *seq.*, 232

B

von Babo, 206, 207
Bagster, 339
Baker, 369
Balcom, 451
Baly, 244
Barnes, 91
Bayliss, 398
Baynes, 103, 461
Beckmann, 212, 355
Begeman, 51

Bergius, 335, 338
von Berneck, 507
Berthelot, D., 106
Berthelot, Marcellin, 133, 185 *seq.*,
352, 458, 460
Berthollet, 132
Bertrand, 121
Berzelius, 130
Bigelow, 477
Billiter, 403, 414
Biot, 121
Blagden, 212
Blanksma, 432
Bodenstein, 140-144, 146-151, 156,
164, 167, 478, 497 *seq.*
Bodländer, 113
Boltzmann, 42, 44
Bonz, 191
Boyle, 5, 6, 8, 10, 73 *seq.*, 90, 95,
193 *seq.*
Braun, 136
Braume, 479
Bredig, 264-266, 300, 302, 303,
325, 394, 397, 400, 401, 418,
451, 469 *seq.*, 479 *seq.*, 501 *seq.*,
508 *seq.*
Brooks, 496
Brown, 21, 401
Bruner, 385-387, 477, 492 *seq.*
Bruni, 335, 347
Brunner, 493, 494, 508
de Bryer, Lobry, 400, 469
Bunsen, 456
Burke, Miss, 333

Burton, 404 *seq.*, 413 *seq.*
Byk, 1

C

Cailletet, 85, 106, 122
Carrara, 333, 335
Carrol, 331
Cash, G., 205
Caspari, 398, 416
Centnerschwer, 339
Charles, 5, 6, 73, 193
Chwolson, 98
Clausius, 14, 17, 111 *seq.*, 233
Cohen, 333
Colardeau, 122
Collie, 66, 71
Coppet, 213
Crafts, 502
Cripps, 80, 104
Cruikshank, 456
Cuthbertson, 15, 16

D

Dalton, 169, 202, 352
Davies, 342
Deacon, 159, 165, 166, 168, 176
Debray, 133
Denham, 293, 297, 502 *seq.*
Dennison, 257
Desch, 347
Deville, 133
Dieterici, 113 *seq.*
Diethelm, 503
Dixon, 466, 467
Dolezalek, 144
Donders, 199
Donnan, 333, 398, 399, 400,
419 *seq.*, 442, 475
Dorochewski, 219
Drucker, 269, 271
Drude, 12

Dumas, 125
Dutoit, 331

E

Einstein, 1, 15, 28, 30, 31 *seq.*, 38,
56
Ekenstein, 469
Eötvös, 125
Esson, 133
Euler, 468
Eykmann, 216

F

von Falckenstein, 152 *seq.*, 163, 166
Faraday, 223, 224, 506
Farmer, R. C., 300, 303
Farrow, 416, 417
Federlin, 453
Fick, 421 *seq.*, 490
Finck, 144
Findlay, 68, 254, 375
Fletcher, 56
Flugel, 270
Fock, 344
Förster, 503
Fraenkel, 300, 470 *seq.*
Franz, 58
Frazer, 204
Freundlich, 410, 418, 420, 507
Friderich, 331
Friedel, 502
Friend, N., 61
Fulhame, 466

G

Gaus, 257
Gay-Lussac, 5, 6, 73, 90, 152, 193,
199 *seq.*
Geiger, 51, 144
Geissler, 347

Getman, 239
 Gibbs, 506
 Godlewski, 333
 Goldschmidt, H., 470, 473, 476,
 479, 481 *seq.*
 Goodwin, 381
 Gouy, 22, 30, 401
 Graham, 395-398
 Groves, 133
 Guldberg, 106, 133, 134, 216

H

Haber, 122, 144, 145, 152, 164,
 167, 505
 Hamburger, 199
 Hantsch, 317, 318, 335
 Harcourt, 133
 Hardy, 403, 409, 413, 417, 420
 Harris, 399
 Haskell, 421 *seq.*
 Hauer, 341
 Helmholtz, 404, 407
 Henri, V., 399, 414, 415, 488
 Henry, 203, 349, 354-356
 Henry, P., 185
 Hertz, 121, 122
 Herz, 359
 Herzog, 503
 Hess, V., 220
 Heydweiller, 324, 325, 330
 Hittorf, 252, 338
 Hoff, van 't, 24, 25, 129, 134, 187,
 194-217, 231-237, 272 *seq.*, 330,
 345, 352, 354-356, 440, 442, 447,
 464, 501
 Hoffmann, 125
 Holland, W. H., 205
 Holleman, 449
 Horstmann, 216
 Hudson, 325, 327-329, 510

I

Isambert, 365

J

Jahn, H., 270
 Jeans, 1, 14, 17, 19
 Jellinek, 144, 168
 Johnson, F. M. G., 369
 Jonhonnot, 14
 Jones, H. C., 219, 220, 239, 331,
 334, 335
 Jones, W. J., 187 *seq.*, 458
 Joule, 10, 11, 74
 Judson, 441
 Just, 442

K

Kahlenberg, 336, 339
 Kanolt, 325
 Kendall, 255, 273
 Knietsch, 167
 Knoblauch, 457, 458
 Knox, 387
 Knudsen, 122
 Koelichen, 468, 469
 Kohlrausch, 220, 225, 227-231, 239,
 245, 252, 254, 256, 257, 261, 270,
 272, 301, 324, 325, 334
 König, 443
 Krafft, 420
 Kremann, R., 191
 Kuenen, 12, 96, 111
 Kuriloff, 363
 Kurlbaum, 51

L

van Laar, 369
 Lamb, 404 *seq.*, 414
 Lamble, 462
 Langmuir, 151
 Lapworth, 187 *seq.*, 458, 478
 Le Chatelier, 136, 151, 364
 Le Rossignol, 152, 442
 Leduc, 108
 Lehfelddt, 135

Lehmann, 341
 Lemoine, 140
 Lewis, G. N., 152, 166, 260, 340
 Lewis, W. C. McC., 12, 14, 103,
 399, 402, 408, 414, 462
 Ley, 299, 300
 Lichty, 481
 Lindemann, F. A., 58
 Linder, 403, 409, 411
 Lippman, 14, 405, 418
 Lodge, Sir O., 224, 256
 Lorentz, 22
 Löwenherz, 325
 Löwenstein, 151
 Lummer, 22
 Lunden, 266
 Lunge, 159, 160 *seq.*
 Luther, 442

M

Makower, 70
 Malaguti, 132
 Manchot, 503
 Marc, 495
 Marggraf, 132
 Marmier, 159, 160 *seq.*
 Masson, J. I. O., 394
 Mathias, 85, 106
 Maxwell, J. Clerk, 2, 3, 15, 17
 Mayer, 60
 McDougall, 442
 McGowan, 394
 Meldrum, 238
 Mellor, 129, 151, 444, 447, 453, 469
 Mendeléef, 61, 219
 Menschutkin, 476
 Menzies, 122, 210
 Merton, 244
 Meyer, O. E., 1, 9, 15, 461
 Meyer, Victor, 125, 151, 156
 Millar, 479, 480
 Miller, Lash, 257
 Millikan, 1, 19, 28, 50, 52 *seq.*, 56,
 57
 Mohr, 381

Moore, B., 398
 Morley, 122
 Morse, 204-206
 Morton, W. B., 47
 Mosotti, 14
 Müller, 420
 Myers, C. N., 205

N

Natanson, 151
 Nernst, 4, 58, 121, 144, 151, 156,
 168, 222, 237, 238, 271, 325,
 330, 335, 352 *seq.*, 375, 376, 379,
 380, 390, 418, 421, 423, 429, 477,
 491, 493 *seq.*, 508
 Nicholson, 62 *seq.*, 71
 Noyes, 260, 269, 325, 340, 390 *seq.*,
 423, 441, 490 *seq.*, 496

O

Oberbeck, 18
 Oberer, 503
 Ohm, 223, 230
 Öholm, 427, 428
 Onnes, 104, 123
 van Oordt, 152
 Osaka, 328
 Ostwald, Wilhelm, 227, 243-245,
 262 *seq.*, 275, 282, 286-291, 307,
 308, 310, 318-320, 323, 325,
 333, 334, 339, 376, 394, 447,
 475, 478
 Ostwald, Wolfg., 420
 Oudemann, 242, 243

P

Palmaer, 246
 Parrot, 192
 Partington, 273
 Patterson, 66, 71, 80, 104
 Peddle, 239

Perman, 43, 342
 Perrin, 1, 15, 21, 22 *seq.*, 36 *seq.*,
 39, 47, 51, 56, 401
 Pfeffer, 24, 25, 192 *seq.*
 Picton, 403, 409, 411
 Planck, 22, 51
 Pockels, 401
 Pohl, 152
 Porter, A. W., 121, 479
 Poynting, 13
 Preuner, 151
 Price, 453
 Pringsheim, 22

Q

Quincke, 12, 402

R

Ramsay, Sir William, 21, 43, 63,
 70, 90 *seq.*, 100, 101, 120 *seq.*,
 125 *seq.*, 335, 401, 409, 435
 Rankine, A. O., 9, 16
 Rankine, W. J., 121
 Raoult, 207 *seq.*, 235
 Raveau, 111
 Rayleigh, Lord, 18
 Regener, 51
 Reinganum, 12
 Reinold, 13
 Richardson, A., 151
 Richardson, O. W., 58
 Ritzel, 495
 Rivett, 339
 Riviere, 122
 Roaf, 398
 Roscoe, 221, 456
 Rose-Innes, 43
 Roshdestwenski, 219
 Rothmund, 394
 Rücker, 13
 Rudolphi, 271 *seq.*, 333
 Rudolf, 80

Rüdorff, 213
 Rümelin, 435
 Rutherford, 51, 59, 63, 70, 433 *seq.*,
 439, 455, 496

S

Sacerdoti, 108
 Schlundt, 336
 von Schmoluchowski, 39
 Senter, 479, 508, 509
 Sherrill, 391, 392
 Shields, 125 *seq.*, 294, 325, 329,
 335
 Siedentopf, 399
 Skraup, 450, 451
 Smith, A., 122
 Snethlage, 479
 Soddy, 21, 68, 70, 433 *seq.*, 455
 Soret, 200
 Spencer, 503
 Speranski, 342
 Spitalski, 471
 Spohr, 463
 St. Gilles, 133, 185 *seq.*, 460
 Starck, 151, 156
 Steele, 339
 Stern, 472
 Stieglitz, 390, 394
 Stokes, 28, 32, 33, 55, 408
 Strutt, 170
 Sutherland, 12, 19
 Svedberg, 1, 39, 397

T

Tammann, 98, 201, 204
 Taylor, H. S., 339
 Teletow, 501-503, 508
 Thomsen, 286, 287
 Thomson, James, 87 *seq.*, 97
 Thomson, Sir J. J., 13, 28, 44 *seq.*,
 58, 59 *seq.*, 62, 63, 64, 237, 238,
 330, 335, 401, 477, 506

Thomson, Sir William (Lord Kelvin), 10, 11, 18, 210
 Tizard, 297, 309 *seq.*
 Tolloczko, 492 *seq.*
 Tolman, 251
 Townsend, 57, 67, 439
 Traube, I., 192
 Trautz, 495
 Turner, 238, 239
 Tyndall, 396, 399

U

Udby, 482

V

Valson, 241
 Vanstone, 342
 de Vries, 196, 204

W

Waage, 133, 134
 Waals, J. D. van der, 11, 12, 16, 17, 78, 94 *seq.*, 121 *seq.*, 126
 Waddell, 184
 Wagemann, 333
 Walden, 80, 238, 331, 332 *seq.*
 Walker, James, 146, 266, 287, 297, 303, 318 *seq.*, 339, 389, 441, 471
 Walton, 471
 Warder, 438, 464

von Wartenberg, 151
 Wason, 441
 Wedekind, 495
 Wegscheider, 369, 449 *seq.*
 Wheatstone, 225
 Whetham, 256, 411
 Whitney, 490 *seq.*, 496
 Whytlaw-Gray, 70, 80, 104
 Wiedeman, 58
 Wiener, 18
 Wijs, 325, 327, 468
 Wildermann, 333, 495
 Wilhelmy, 130-132
 Will, 469
 Wilson, C. T. R., 47, 48
 Wilson, H. A., 48, 49
 Wislicenus, 318
 Wöhler, 506
 Wood, R. W., 62
 Woudstra, 416, 417
 Wüllner, 207

Y

Young, S., 80, 85, 86, 90 *seq.*, 100, 101, 104, 109 *seq.*, 120 *seq.*

Z

Zaitschek, 191
 Zawadzki, 385
 Zinn, J. B., 205
 Zsigmondy, 399, 401, 420

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